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The pollution history of two urban lakes in Coventry, UK

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THE POLLUTION HISTORY OF TWO URBAN LAKES IN COVENTRY, UK

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Abstract

Human society has influenced the environment for at least the last 15000 years but, since the Industrial Revolution, the resultant environmental impacts have become more widespread. Lake and reservoir bottom-sediments have been widely used in many studies for reconstructing this impact over medium timescales (tens to hundreds of years). Few long-term studies of hydrological change exist and sediments are useful as surrogates for direct monitoring since they are sensitive to change within the catchment. This study uses the properties of urban lake sediments in order to reconstruct environmental pollution history.

The two principal objectives of this study were the reconstruction of historical atmospheric, point source and diffuse heavy metal pollution in an urban environment and the evaluation of the lake-sediment record as a source of proxy hydrological data over the last 100-150 years.

A paired lake-catchment study was undertaken by comparing the records contained in a closed and an open lake. The closed lake (Swanswell Pool) is situated in the centre of the city of Coventry where the main source of pollution is atmospheric. This site provides a contrast to an open basin (Wyken Pool) with a multi-source catchment in addition to an atmospheric influx.

Trends in urban lake sediment cores indicate increasing heavy metal concentrations upcore, with cultural enrichment factors for individual heavy metals of between 55.4 and 2.6. Storage of heavy metals in the catchment of the closed basin

were significant, although it was found that up to 85% of the Zn and 90% of the Pb were actually stored in the lake sediments. Catchment sources contributed up to 5 times more than the atmosphere in the Wyken Slough catchment. Heavy metals budgets were calculated, and these showed that loadings of metals have increased by up to 7.5 times between 1850 and the present day. Sequential digestion of the lake sediments at both sites showed that the important fractions containing heavy metals were Fe and Mn oxides and organic matter. The heavy metals associated with these fractions could be remobilised with changing environmental conditions, but an analysis of contemporary water quality indicated that, at present, suitable Eh and pH conditions for remobilisation did not occur.

It was concluded that these urban lakes do preserve the heavy metals record and can provide surrogate data on medium-term environmental change. However, the complex mixture of materials associated with urban sedimentation resulted in a lack of correlation between heavy metals and mineral magnetic properties in either lake, and in the catchment of Wyken Slough. Hence mineral magnetic properties of sediments in urban catchments do not appear to be a suitable surrogate for heavy metals analysis.

Urban lakes appear to provide a much-neglected opportunity for palaeolimnological reconstruction over a period when little directly monitored data exists.

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Chapter 1

1.1 Introduction

"..human activity has been and will continue to be a major extrinsic force of change."

Starkel *et al.* (1991) p 521

This study is concerned with the detection of change in the environment. The observation by Starkel *et al.* (1991) above, highlights an important force of change in the natural environment; that of the activities of mankind. The importance of the role of human beings in environmental change has taken time to assume its present significance. Until the 1950s and 60s Physical Geographers tended to focus on changes to the environment before human activity or

"..at best to include man as an afterthought or an appendage."

Gregory (1985) p 116.

However, the impact of human activities has now

"..come prominently into focus and (is) a major concern of scientific endeavour."

Thornes & Gregory (1991) p 522.

This scientific endeavour has profited from the drive in the 1980s to understand the impact of climate change brought about by anthropogenic activity (Gregory, 1991). Associated with

this has perhaps come the realization that the whole field of human influence needs to be assessed, enabling suggestions to be made as to how this influence may best be controlled.

1.2 Timescales

Humans have influenced the environment for at least the last 15000 years and there have been many palaeohydrological studies concerned with the late glacial and Holocene in which the human impact has been identified. The International Geological Correlation Programme (IGCP) Project 158 is an example of a long to medium timescale study of the magnitude of human impact over the last 15000 years on fluvial systems and the environmental changes recorded in lakes, mires and their contributing catchments (IGCP Subprojects A and B; Berglund, 1983). Chapter 2 of this thesis outlines many other such long to medium timescale projects in which attempts have been made to reconstruct Quaternary events and environments.

A second approach to the study of the impact of human activity on environmental systems, working in parallel with long-term reconstruction, is the measurement of contemporary hydrological processes in experimental catchments. Lewin (1980) defined this as the "*eclectic*" phase of geomorphology in which the two factions studied past and present in isolation from one another and is exemplified by the work of Gregory & Walling (1973), Burt & Walling (1984) Hadley (1985) and Roberts (1989). The observation of contemporary events is necessarily curtailed by the length of the research project from as little as a field season to "the few years of 'PhD

time'" (Lewin, 1980 p 5). Problems associated with the investigation of contemporary processes include the lack of knowledge of antecedent catchment conditions. Monitoring of a pollution problem after the event makes it difficult to assess the seriousness of the impact on the environment as the conditions prior to the event are not known:

"...extensive monitoring of various aspects of environmental pollution was generally not carried out until after the major problems were identified."

Foster and Dearing (1987b) p 173

There is, therefore, a need for an approach which evaluates human impacts at intermediate timescales, lying between that covered by palaeohydrological reconstruction and the data generated by contemporary monitoring. Petts (1989) characterised the period between 100 and 500 years ago and the present day as being the time of increasing human impact on rivers and hence on the lakes within their drainage basins. This present study covers part of the timescale of greatest human influence on the environment by focusing on the past 150 years. The importance of this period is shown by the Industrial Revolution; the industrial and technological advances of which touched every aspect of the biosphere and hydrosphere.

Whilst there are many studies of lakes and the effects of human intervention in the natural environment (Elner & Happey-Wood, 1980 ; Hamilton-Taylor, 1979, 1983; Batterbee *et al.*, 1988) there are few which have investigated any sites at the

focal point of industrialisation and urbanisation; the urban lake. Many studies have examined the temporal distribution of atmospheric pollutants by examining the heavy metal content of lake sediment cores taken from remote sites, such as those undertaken by Verta *et al.* (1989), in sparsely populated areas of Finland and polar ice cores in the Northern Hemisphere (Nriagu *et al.*, 1979). There are also studies of the atmospheric contribution of pollutants to lowland rural and semi-rural lake sediments, such as those undertaken in North Warwickshire (Foster and Dearing, 1987) and in south central Wales, (Jones, 1984; Jones *et al.*, 1978, 1985). This present study concentrates on lakes proximal to the industrial and urbanised areas responsible for the production of atmospheric pollutants.

1.3 Aims and Objectives

This research project was designed in order to meet two basic aims:

1. To reconstruct the history of pollution in an urban environment

2. To evaluate the lake sediment-record as a source of proxy hydrological data over the last 100-150 years.

In relation to the above aims, the following specific objectives were identified:

1.1 To quantify the historical changes in atmospheric pollution as recorded in urban lakes

1.2 To quantify the historical changes in the heavy metal content of lake sediment derived from a slowly industrialising catchment over the last 150 years and to identify the role of the drainage basin in the sediment delivery process.

1.3 To quantify the relative contribution of atmospheric and catchment derived contaminants.

2.1 To evaluate the use of paired lake-catchments in reconstructing change over short to medium timescales

2.2 To identify the practical limitations of utilising a range of environmental tracers (heavy metals, environmental magnetism and radioisotopes) for reconstructing pollution histories and identifying contaminant sources.

1.4 Structure of the thesis

The first section of Chapter 2 justifies the use of lake catchments and, specifically, the paired lake-catchment approach adopted in this study. Sections 2.2 to 2.4 address the use of a lake-sediment based approach to reconstruct the history of a lake basin over a time period of around 150 years. Section 2.5 gives the justification for the selection of sites, particularly in terms of the value of using closed and open basins for comparative purposes. Sections 2.5 to 2.9

explain the methodological framework applied to this study of urban lake pollution.

Chapter 3 describes the two sites in detail, using historical documents to reconstruct site histories. The results of sediment sampling and laboratory analysis are presented in Chapters 4 to 6. Chapter 7 attempts to construct heavy metal budgets for both sites and then to set them in a framework in which a gradient of atmospheric pollution from urban to rural sites is quantified. The discussion, presented in Chapter 8, summarises the degree to which the foregoing aims and objectives have been achieved.

Chapter 2

The Conceptual and Methodological framework

2.1 Introduction

This chapter explains the rationale behind the present study by examining previous work carried out in the broad fields of catchment hydrology, limnology and palaeolimnology. It explains the use of heavy metals, in terms of the properties which make them suitable for such a study, and also explores the methodology and techniques chosen in terms of their suitability and past application. The chapter considers the following:

1. The use of lake sediments in the reconstruction of past environments.

2. The use of lake sediments in reconstructing the history of anthropogenic pollution.

3. The chemical properties of heavy metals in the context of their suitability for reconstructing pollution history.

4. The sites selected for this research project.

5. A critique of the methodology employed in sampling and analysis of lake and other sediments.

2.2 Lake-catchment based studies.

The study of lakes and their drainage basins can provide two types of important information; firstly, contemporary process-based monitoring of change in the short term (years to decades) and, secondly, the study of longer term change (decades to centuries) by analysis of deposited sediment. Direct observation of an active system enables modelling of several aspects of environmental behaviour (eg. Hadley, 1985; Roberts, 1989). Reconstruction of past events permits an assessment of the impact of change within the catchment, but cannot provide a resolution high enough for the data to be used as a substitute for monitoring. The advantages and disadvantages of various monitoring and reconstruction strategies employed to quantify change in catchment systems are briefly considered in the following sections.

The Hubbard Brook study (Bormann & Likens, 1969) originated the idea of the ecosystem-watershed concept in which a study of the integration of various ecological, meteorological and hydrological processes was attempted within a single drainage basin, water being the linking factor. O'Sullivan (1979a), in his review of the ecosystem-watershed concept, emphasised the importance of the interdisciplinary nature of this study:

"The ecosystem-watershed concept is thus capable of providing a conceptual framework for interdisciplinary studies of the dynamics and processes of contemporary environments."

O'Sullivan (1979 a) p 273

However, even though contemporary process monitoring of this kind can take account of the impact of society on the catchment, these data are only available for a relatively short time span (discussed further in section 2.3). Since atmospheric pollution, for example, has been affecting the environment for at least the past 130 years (Norton, 1986), longer term data are needed to reconstruct catchment pollution history. Sediment accumulating within the catchment in rivers, lakes and on floodplains will incorporate heavy metals and will potentially contain evidence of such pollution through time. The following section considers the relative merits of fluvial, limnic and alluvial deposits in retaining this evidence.

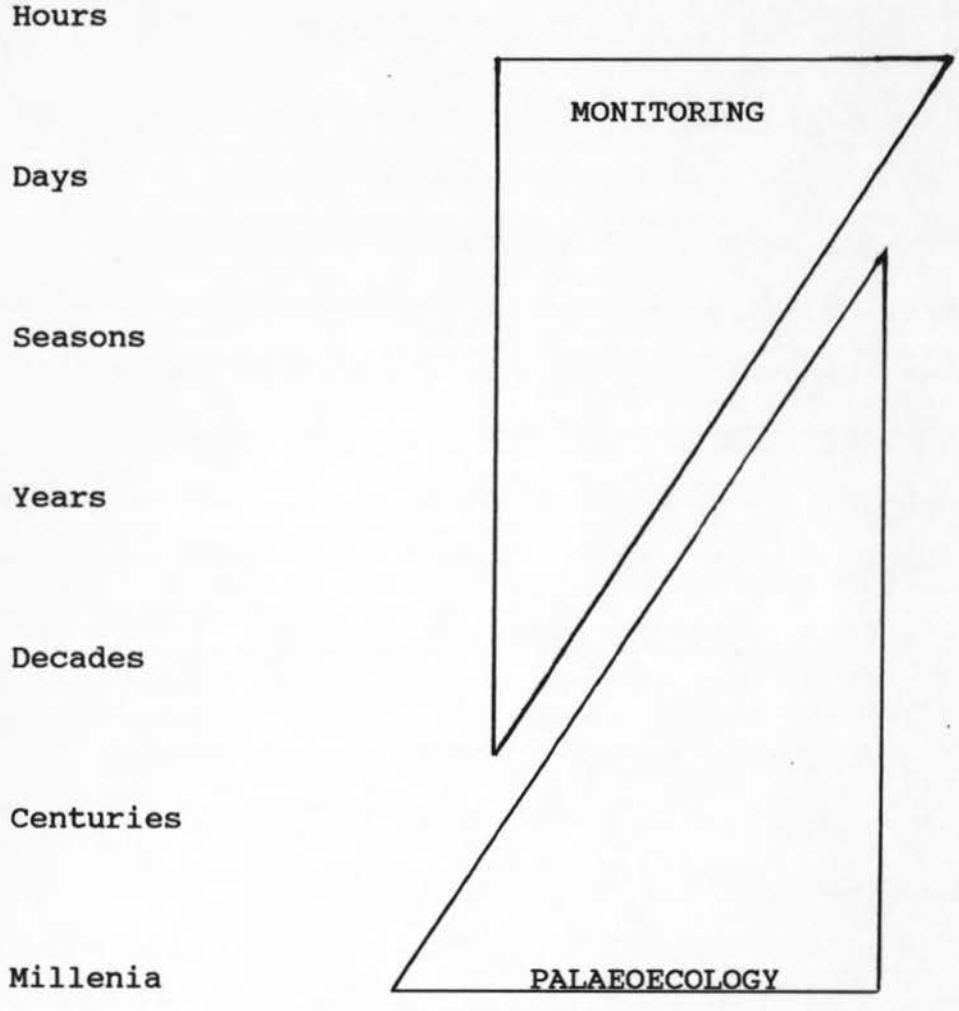
Lewin (1987), assessed the patterns of change within the course of the River Severn and found that the channels exhibited marked changes spatially over time. Hence sediment deposited in the channel will also change spatially with time. Förstner's (1983), critique of the use of river water samples to establish trends in aquatic pollution, highlights problems which also might be associated with the use of river sediments, principally those of fluctuations in daily and seasonal flows which will directly impact on the depositional

or transportational regime of the river. River sediments thus represent a means of monitoring pollution on a timescale of hours to decades (Fig 2.1) rather than a means of reconstructing pollution history.

Alluvial deposits represent inundation of the floodplain and deposition of fine sediment (Macklin, 1992). They therefore do not represent a continuous sedimentary sequence necessary for the reconstruction of pollution history of a catchment. There are few studies dedicated to long term monitoring of river sediments and alluvial deposits. A review of these studies is beyond the scope of this thesis, but is presented in Foster & Charlesworth (1995).

Atmospheric deposition of pollutants onto land can contaminate soils, but their heavy metals record is a transient one (Foster & Charlesworth, 1995). The soil profile is dominated by pedogenic processes and interactions with plants (Mattigod & Page, 1983). It is therefore dynamic and the distribution of heavy metals in the profile reflects these processes rather than historical accumulation of pollutants sequentially. Soils, however, are subject to erosion and, if they are contaminated with heavy metals, may provide secondary, non-point sources of pollution in the hydrological cycle. The analysis of soils, therefore, does not provide a means of pollution history reconstruction, although soils are an important sink and, ultimately, source of heavy metals in the fluvial system.

Fig 2.1 Comparison of the timescales of environmental monitoring and palaeoenvironmental reconstruction (after Smol, 1992)



Lake sediments on the other hand

"..potentially contain a tremendous 'library' of information."

Smol (1992) p 50

The use of lake sediments as proxy hydrological data are the subject of detailed review in section 2.3.

Most studies or "experiments" (Deevey, 1969; Church, 1984) of this kind use historical reconstruction as a proxy means of monitoring the effect of catchment disturbance on the system. They do not involve the intentional interference with the landscape which would produce inarguable results. Most catchment studies, therefore, show little evidence of experimental control. They are, however

"..an essential part of the complete enquiry that develops conceptual understanding."

Church (1984) p 571.

A means of exerting some experimental control in lake-sediment based studies is in the use of a paired lake-catchment approach. This can introduce background control and, hence, improve scientific understanding (Foster *et al.*, 1987). Many studies have been carried out using paired catchment studies, for example in the English Midlands (Foster *et al.*, 1987) and elsewhere (Hewlett, 1967, in Coweeta, USA; Fuehrer, 1993, in Hesse, Germany). A paired lake-catchment study,

coupled with a multiple coring exercise, can provide data which allow long term responses of the environment to pollution from different sources to be quantified. Antecedent catchment conditions can be obtained from an analysis of the sediments prior to the period of interest. The lake sediment records can be used to quantify the responses of the catchment to change, the likelihood of recovery without further interference, and the chances of reinstatement if the catchment is actively managed.

The lake is therefore highly sensitive to changes within the catchment and this is reflected in the sediments, the use of which in historical reconstruction is considered in the next section.

2.3 The use of lake sediments in historical reconstruction

Mackereth (1966) was the pioneer in the UK on the use of lake sediments to infer environmental change. This work in the English Lake District was followed by other research, notably by Pennington (1973), who focussed on the environmental changes in the same area recorded in the upper 30 cm of sediment from Lake Windermere. Pennington described the sediment column as

"...the continuously accumulating column of lake sediment as a medium within which environmental changes are recorded in sequence, including recent changes attributable to Man."

Pennington (1973) p 363

In 1977, Oldfield proposed that

"Lake sediments provide an exceptionally full record of the medium to long term effects of modern technology on environmental systems." Oldfield (1977) p 496

Further research has indicated that lake sediments can be looked upon as a "bank" of environmental information (Håkanson & Jansson, 1983). The record contained within lake sediments can help discriminate between polluted and unpolluted environments, identify spatial and temporal patterns of such impacts and help to identify the nature and relative importance of individual contaminants.

Håkanson & Jansson (1983) identified four factors responsible for sedimentation in lakes. These include internal productivity, trap efficiency, the ability of upstream components of the catchment to hold sediment, and therefore limit supply, and the relative contributions of allochthonous material from direct drainage basin inputs.

Lake sediments are not a sterile medium, but support micro- and macro-organisms which affect the incorporation of contaminants into the sediment, their subsequent stability

and, hence, their concentration and distribution with depth in the sediment column. Cline & Upchurch (1973) suggest that the movement of metals in the biotic zone (the upper 10 cm of the sediment column) occurs as the metals form a film around gas bubbles in the sediment and are moved upwards through the sediment on the bubble of gas. Bacteria may also selectively take up heavy metals and mobilise them in the sediment. However, as Förstner & Wittmann (1981) suggest, there is little quantitatively known about the effects of bioturbation and Håkanson & Jansson (1983) conclude that the processes are too complex to be able to describe mathematically.

Trap efficiency is a reflection of the ability of the lake basin to trap and retain sediment. It is dependent on several factors including the density gradient between the lake water and the inflowing streams, the position of any thermocline or pycnocline and the chemistry of the lake water which may inhibit settling due to flocculation (Foster *et al.*, 1990). There are several models which can predict trap efficiency and these are reviewed by Foster *et al.* (1990). These include models based on basin area (Brown, 1944), the capacity inflow ratio (Brune, 1953) and the capacity inflow / particle size relationship (Chen, 1975; Heinemann, 1984; Rausch & Heinemann, 1984). A further model is proposed by Moglen & M^{c} Cuen (1988) in which trap efficiency is related to sediment movement and is related to the proportion of the inflowing sediment retained by the basin:

$$E_t = \frac{q_{si} - q_{so}}{q_{si}} = \qquad \text{(Equation 2.1)}$$

Where E_t = trap efficiency

q_{so} = sediment carried in the outflow

q_{si} = sediment carried in the inflow

In the case of urban lakes, three problems of assessing trap efficiency by these methods are apparent:

1. Urban lakes often do not have a contributing catchment from which to estimate either the basin area or the inflow. The lack of direct inflow or outflow information makes estimation of suspended sediment trap efficiency difficult.

2. Where the urban lake does have a catchment, the act of urbanisation introduces an artificial drainage network into the system which routes surface runoff from a greater area into the lake (Packman, 1980; Uehara, 1980). This improved drainage changes not only flow volumes but also flow characteristics, so that the storm hydrograph response is quicker with higher peak discharges for even small storm events (Packman, 1980). This impacts on basin area, capacity inflow and particle size relationships, due to increased discharge.

3. Sediment delivery to the lake is not constant. The study by Wolman (1967) showed that suspended sediment yields increased in a catchment subjected to the disturbance associated with urbanisation and industrialisation. In a large urban area, land clearance and construction may be almost continuous as small parts are disturbed each year (Douglas, 1985). In between each period of increased fluvial sediment yield, the levels may fall back to those before urbanisation (Wolman, 1967).

Estimation of trap efficiency of urban lakes is therefore fraught with difficulty which current models cannot address and whilst an important consideration under normal circumstances, the unique conditions of urban lakes with respect particularly to catchment-isolation, canalisation and frequent periods of disturbance means that this problem is not considered in any great detail in this study.

Håkanson & Jansson's (1983) third control on sedimentation was the influence of upstream sediment traps which may prevent some of the suspended load reaching the lake. For the purposes of this study, the influence of marshland is important, this is considered in greater detail in section 2.8ii where the characteristics of the specific research sites are discussed.

Håkanson & Jansson (1983) lastly identify a "load" factor which controls sedimentation in lake basins. This identifies that there are mainly two sources of material from outside the lake; firstly, allochthonous, or catchment-derived material

transported as bed and suspended load, and, secondly, the anthropogenic contribution. Section 2.7 justifies the choice of the research sites in terms of discriminating these, and also in terms of discriminating the atmospheric component of the anthropogenic contribution.

Sediment cores retrieved from a body of lake mud are site specific and can therefore provide data concerning the history of the catchment from which they are derived. This is valuable when formulating management strategies. Once a management problem has been identified, and the threat of the problem with regard to recreation, wildlife or the aesthetics of an environment has been recognised, lake sediment studies can yield results faster than process-based observations and can often be more cost-effective. Oldfield & Clark (1990) designates this a "post-hoc" contribution to scientific methodology. Sediment-based studies can therefore give a more complete picture of the variability, recurrence and trends of pollution events in a far shorter time and over a longer period than process based observations.

Only a fraction of the chemical load transported by a stream are in the dissolved phase. Clays, silts and organic matter all provide large surface areas over which sorbtion of pollutants may occur. Indeed, suspended sediments often provide the transport mechanism for many chemical constituents (Feltz, 1980). The average length of contemporary records for the study of chemical transport processes in fluvial systems are usually no more than 5 years; leaving the data open to

bias by extreme hydrological or pollution events. Lake sediments, in contrast, provide an opportunity to analyse the suspended load not only contemporaneously but also historically.

The longer time scale over which pollution can be assessed using lake sediment records provides a means of establishing the effects of secular variations, of demonstrating the preceding conditions leading to the concerns of the present as well as providing historical data from which to extrapolate trends and rates of change (Oldfield & Clark, 1990).

As in this study, multidisciplinary analysis of lake sediments can yield integrated reconstructions of the history of the catchment in terms of the interactions occuring between ecology, culture and changes in technology. As Oldfield & Clark (1990) point out, the limitation of using lake sediments alone is in the narrowness of disregarding interactions occurring in the rest of the catchment system. The present study attempts to redress this imbalance by examining the sources and sinks of contamination associated with the atmosphere, fluvial systems and the soil and hence to gain some insight into the relative importance of these sources and stores within the whole fluvial system.

2.4 The use of lake sediments to assess anthropogenic heavy metal pollution.

As a result of urbanisation, mining and industrialisation since the Industrial Revolution, the environment has become polluted with the wastes and by-products of the processes involved.

Lake sediments have been widely used as indicators of both contemporary and historical pollution. This is because both natural and manmade lakes are often located in areas of intense development. Often the threat of pollution becomes more serious when the lake is used as a source of potable water. Förstner & Wittmann (1981) illustrate the importance of analytical studies of sediment cores in palaeolimnological reconstruction of pollution :

"During the last 2 decades, sediment analysis has aquired a new dimension by being employed as a tool to trace manmade pollution influences in inland and coastal waters."

Förstner & Wittmann (1981) p 140

The concentration of the contaminant can also reveal trends in catchment history, such as whether pollution of the water courses entering the lake has changed through time.

There have been a great number of sediment-based research projects carried out in North America and Europe in the last 20 years. The majority of the American studies have been based

on an analysis of sediment cores from the Laurentian Great Lakes, and other lakes and ponds in the United States. These studies have been concerned with the enrichment of such elements as Cu, Zn, Pb, Ni, Cd, Sc, Hg, As, Cr, Sb, Co, Ag, V, La and Be where increases in concentration of these elements towards the mud-water interface has been identified; (Shimp *et al.*, 1971; Leland *et al.*, 1973; Walters *et al.*, 1974; Kemp & Thomas, 1976; Kemp *et al.*, 1976a,b,1978; Kemp & Dell, 1976; Wheeler & Dunning, 1976; Christensen & Chien, 1979; Nriagu *et al.*, 1979; Glooschenko *et al.*, 1981; Goldberg *et al.*, 1981). Workers in Europe, for example Verta *et al.*, (1989), presented a history of heavy metals pollution in Finland from an analysis of lake sediments. In Sweden, Renberg (1986), used sediments dated by their seasonal varves to estimate the effects of industrialisation on six lakes and to assign events in their past histories to fluctuations in the chemistry of their sediments. Förstner, in association with others both in Brazil and Holland, has analysed sediments to assess the catchment history of polluted lakes (Förstner, 1976; Förstner *et al.*, 1979; Förstner & Wittmann, 1981; Förstner & Salomons, 1981a, 1981b).

In the UK, Elner & Happey-Wood (1980) reconstructed the history of two linked Welsh lakes from analyses which included chemical and mineral magnetic stratigraphies. This study indicated that the changes in the catchment due to copper mining in the period between the seventeenth and the end of nineteenth centuries could be identified in the lake sediment

record. Hamilton-Taylor (1979) is one of many working in the English Lake District who attributes the increasing metal content of the lake sediment cores to

"..the atmosphere (*which*) is clearly a major potential source of the sedimentary flux.."

Hamilton-Taylor (1979) p 696

Similar evidence for the increased concentration of heavy metals incorporated in the lake sediments of the UK are given by Harding & Whitton (1978) from the Derwent Reservoir, northern England, Hilton & Gibbs (1984) from Esthwaite Water, the English Lake District and Jones *et al.*, (1978), from Llangorse Lake, Wales. Hamilton-Taylor (1983) presented the results of analysing sediments from six lakes in north west England demonstrating similar trends in enrichment of Cu, Pb and Zn dating from the mid nineteenth century.

These studies illustrate the trend of increasing heavy metal incorporation in the sediments of lakes in several regions of the world over the last 150 years. Research specific to heavy metal pollution in the urban environment has concentrated on the transport of pollutants and their effect on the biosphere. Few of these have been specific to the urban lake, the sink of a great deal of the anthropogenically derived heavy metals. Studies of the urban environment have therefore concentrated on four main components :

1. The sources of pollution, such as road-side gulley pots (Butler, 1979; Förstner & Wittmann, 1981; Colyer, 1983; Beckwith *et al.*, 1984; Gjessing *et al.*, 1984; Yousef *et al.*, 1984; Gibson & Farmer, 1984; Brinkmann, 1985).

2. The transport of anthropogenically derived heavy metal contaminants in urban rivers (Wilber & Hunter, 1979; Samanidou & Fytianos, 1987; Thoms, 1987), and the effects of heavy metal contamination on urban rivers (Keller & Hoffmann, 1977).

3. The effects of heavy metal pollution on biota (Hellawell, 1989; Baudo *et al.*, 1989).

4. Urban lakes (Cherkauer, 1977; Moglen & Mc Cuen, 1988). In both cases the emphasis was on the effect of the lake on the rest of the catchment, rather than the cumulative effects of the upstream catchment on the lake.

Urban lakes are therefore the poor relation in the study of palaeolimnology and historical reconstruction.

The following section outlines the sources of heavy metals in the environment, emphasising the role of industry and urbanisation in their production, transport and redistribution in the environment.

2.5 Heavy metals in the environment

This section outlines the rationale behind the use of heavy metals analysis in the reconstruction of pollution history using lake sediments in four ways :

1. By examining the sources and sinks of heavy metals in the environment

2. By examining the properties of heavy metals in general

3. By discussing the suitability of heavy metals in studies of urban pollution, with particular reference to their modes of transport.

4. By examining the choice of heavy metals used in the investigation to reconstruct pollution history.

i. Sources and sinks of heavy metals in the environment

Fig 2.2 shows the sources of heavy metals to the environment. These can be divided into two broad groups, natural and anthropogenic. The main natural sources are from volcanic and geothermal activity and the process of geologic weathering. The first two are of little significance to the UK, but geologic weathering may release significant amounts of heavy metals from mineralised regions (Fergusson, 1990).

Fig 2.2 Sources of heavy metals in the environment

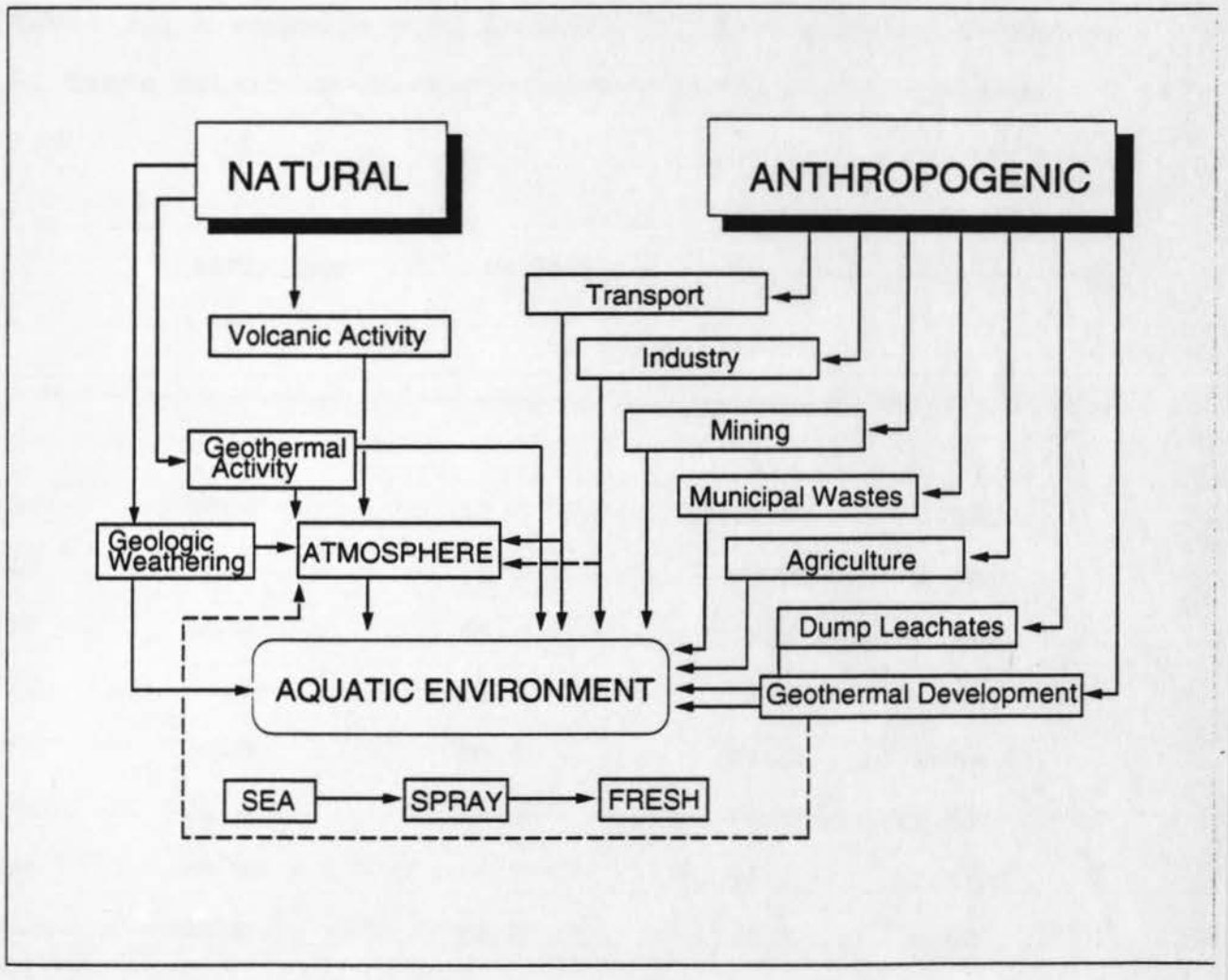


Table 2.1 compares the relative contributions from natural and anthropogenic sources, and shows the overriding importance of society in the global cycling of heavy metals. These figures show that anthropogenic input of heavy metals to the environment is now an order of magnitude higher than natural sources.

Table 2.1 A comparison of natural and anthropogenic emissions of trace metals to the environment, $x10^6$ kg yr^{-1}, (Nriagu, 1990)

	anthropogenic (A)	natural (N)	total	A : N
As	19.0	12.0	31.0	1.58
Cd	7.6	1.3	8.9	5.85
Cr	30.0	44.0	74.0	0.68
Hg	3.6	2.5	6.1	1.44
Ni	56.0	30.0	86.0	1.86
Pb	332.0	12.0	344.0	27.67
Se	6.3	9.3	16.0	3.68
V	86.0	28.0	114.0	3.07

The anthropogenic sources of heavy metals can be further subdivided into two general groups (Brown *et al.*, 1990; Tarr & Ayres, 1990; Macklin, 1992):

1. Those associated with production-related processes. These include mining and smelting, energy generation, manufacturing and agriculture. Brown *et al.* (1990)

2. Those associated with consumption-related processes. These include the use, wear and eventual disposal of consumables and commercial products. The weathering and flaking of paints, the burning of pharmaceuticals, batteries, plastics and electrical goods, the wear and weathering of leather, plastics and surfaces which have been electroplated, and the breaking down and burning of treated wood (Tarr & Ayres, 1990; Brown *et al.*, 1990; Macklin, 1992) Table 2.2 shows the individual heavy metals liberated as a result of each of these processes.

Table 2.3 compares the natural global average contributions of heavy metals to those emitted into the environment from high temperature, production related sources. Brown *et al.* (1990) state that the high temperature processes are those which are the most significant in contributing to atmospheric metal pollution, mainly due to their being emitted in fine particulate or gaseous form. Table 2.3 also illustrates that the relative enrichment of the individual heavy metals to the environment is not equal and that, with the exception of Cd, anthropogenic sources are comparable to,

Table 2.2 Heavy metals released as a result of consumption related activities

---

1. Weathering and flaking of paints and pigments

   Ag, As, Cr, Cd, Cu, Hg, Pb, Zn

2. Burning of

   a.) discarded pharmaceuticals (Ag, As, Cr, Zn)

   b.) batteries (Hg, Cd)

   c.) electronic tubes (Hg)

   d.) plastics (Zn)

   e.) photographic film (Ag)

3. Wear and weathering of

   a.) electroplated surfaces (Cd)

   b.) leather (Cr)

   c.) plastics (Zn)

4. Breaking down and burning of treated wood

   As, Cr, Cu,

Table 2.3 Average annual global trace element conctributions (in thousands of metric tons) to the environment from natural and high-temperature production-related sources (Brown *et al.*, 1990).

	As	Cd	Pb	Se	Hg
Natural					
Dust	0.24	0.25	10.0	0.3	0.03
Volcanoes	7.0	0.5	6.4	0.1	0.03
Forest fires	0.16	0.01	0.05		0.1
Vegetation	0.26	0.2	1.6		
Sea salt	0.14	0.002	0.1		0.003
Total	7.8	0.96	18.6	0.4	0.16
Anthropogenic					
Mining			8.1	0.005	
Smelting non-ferrous metals	15.2	5.3	77.2	0.28	
Fe production	4.3	0.1	50.0	0.01	0.45
Other[1]		0.04	7.2	0.05	
Burnt waste	0.4	1.4	9.0		
P fertilizer	2.6	0.2			
Coal burning	0.5	0.05	13.9	0.68	0.63
Wood burning	0.5	0.2	1.0		
Petroleum combustion			273.0[2]	0.06	0.27
Total	23.5	7.29	439.4	1.085	1.35

[1] Other industrial activities
[2] Pb is introduced into the environment primarily from the use of leaded petrol

or greater than, those from natural sources. Human society is thus the most important factor in the global biogeochemical cycling of heavy metals in the environment (Nriagu, 1990; Macklin, 1992).

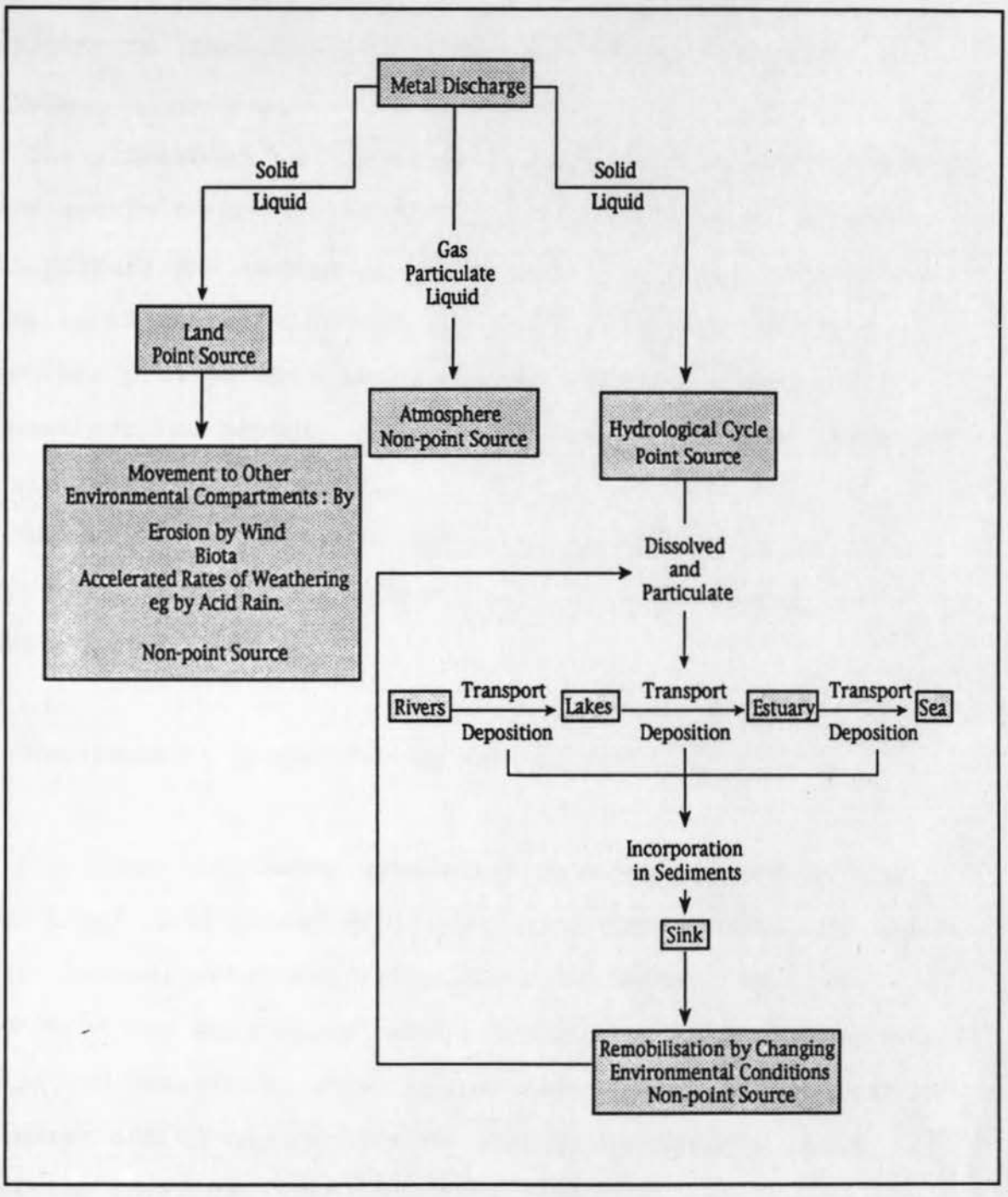
The history of the human use of heavy metals goes back to prehistoric times (Macklin, 1992) when mining and smelting provided the main sources of pollution to the environment. This activity was local or at most regional in impact until the Industrial Revolution since when

"..the production and discharge of trace metals in the environment have been increasing almost at a logarithmic scale."

Nriagu (1990) p 114

The initial discharge of heavy metals into the environment may be through the atmosphere, onto land or directly into the fluvial and limnic systems, but their ultimate dispersal is dependent on the hydrological cycle. The form in which they are released dictates the pathway they take. They may be released in gaseous, particulate, liquid or solid form (Macklin, 1992) and enter the fluvial system in different ways depending on whether they are dispersed from diffuse (non-point) or discrete (point) sources (Mattigod & Page, 1983). Fig 2.3 illustrates the pathways of heavy metals in the freshwater environment from their release to their incorporation in fluvial or limnic sediment. They may remain

Fig 2.3 Pathways of heavy metal transport in the environment



as a sink or be remobilised into other environmental compartments (Macklin, 1992) and thus become non-point sources.

The atmosphere is therefore an important primary source of heavy metals to the environment, but the catchment provides both primary and secondary (remobilised) sources as well as sinks of these trace metals. The sinks of heavy metals therefore provide the focus for studies which attempt to reconstruct the history of heavy metals at the lake-catchment level.

The following sections consider the properties of the heavy metals which facilitate their movement through the aquatic ecosystem.

ii. The chemical properties of heavy metals.

Fig 2.4 shows that heavy metals are generally found in the lower right hand corner of the periodic table. This defines their chemical behaviour (Förstner & Wittmann, 1981), as members of the same group behave chemically in a similar way. Zn and Cd, therefore, often appear together in geochemical processes and Cd may replace Zn in certain enzymes, thus impairing their catalytic function (Manahan, 1993). According to Förstner & Wittmann (1981), metals are characterised primarily by their good conduction of electricity and their electrical resistance which is directly proportional to absolute temperature. Other secondary properties include high

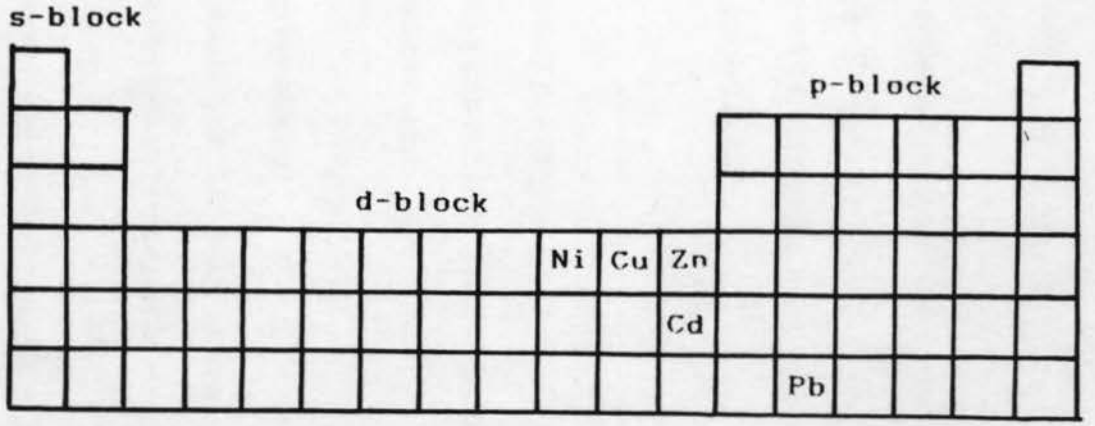


Fig 2.4 The Periodic Table to show the position of Cd, Cu, Zn, Pb and Ni

thermal conductivity, malleability, ductility and high density. It is the property of high density which is mostly used to characterise heavy metals in the environment. Davies (1980), defines the heavy metals as having a density of greater than 6 g cm^{-3}.

Due to their chemical properties and relative abundance in the Earth's crust, heavy metals are:

1. Extracted and frequently used by society
2. Used where living things can come into contact with them
3. Able to significantly disturb the biogeochemical cycle.
4. Toxic to living organisms

(Fergusson, 1990)

Woods' (1974) classification of heavy metals, (in Förstner & Wittmann, 1981), divides them into three categories based on biogeochemical behaviour as:

1. Noncritical to ecosystems
2. Toxic but very insoluble or very rare
3. Very toxic and relatively accessible.

Any study of heavy metal contamination in the environment should therefore pay special attention to the third of Woods categories above as posing the biggest threat to biota. Table 2.4 outlines the densities and crustal abundances of the heavy metals considered in this research project.

Table 2.4 Characteristics of Cu, Cd, Zn, Ni and Pb. From Macklin (1992) after Davies (1980).

	Cd	Cu	Pb	Ni	Zn
1	8.7	8.9	11.3	8.9	7.1
2	0.2	55.0	13.0	75.0	70.0
3		E		E	E
4	P	P	P	P	P
5	3	3	3	3	3

1 = Density (g cm^{-3})

2 = Mean content in crustal rocks (ppm)

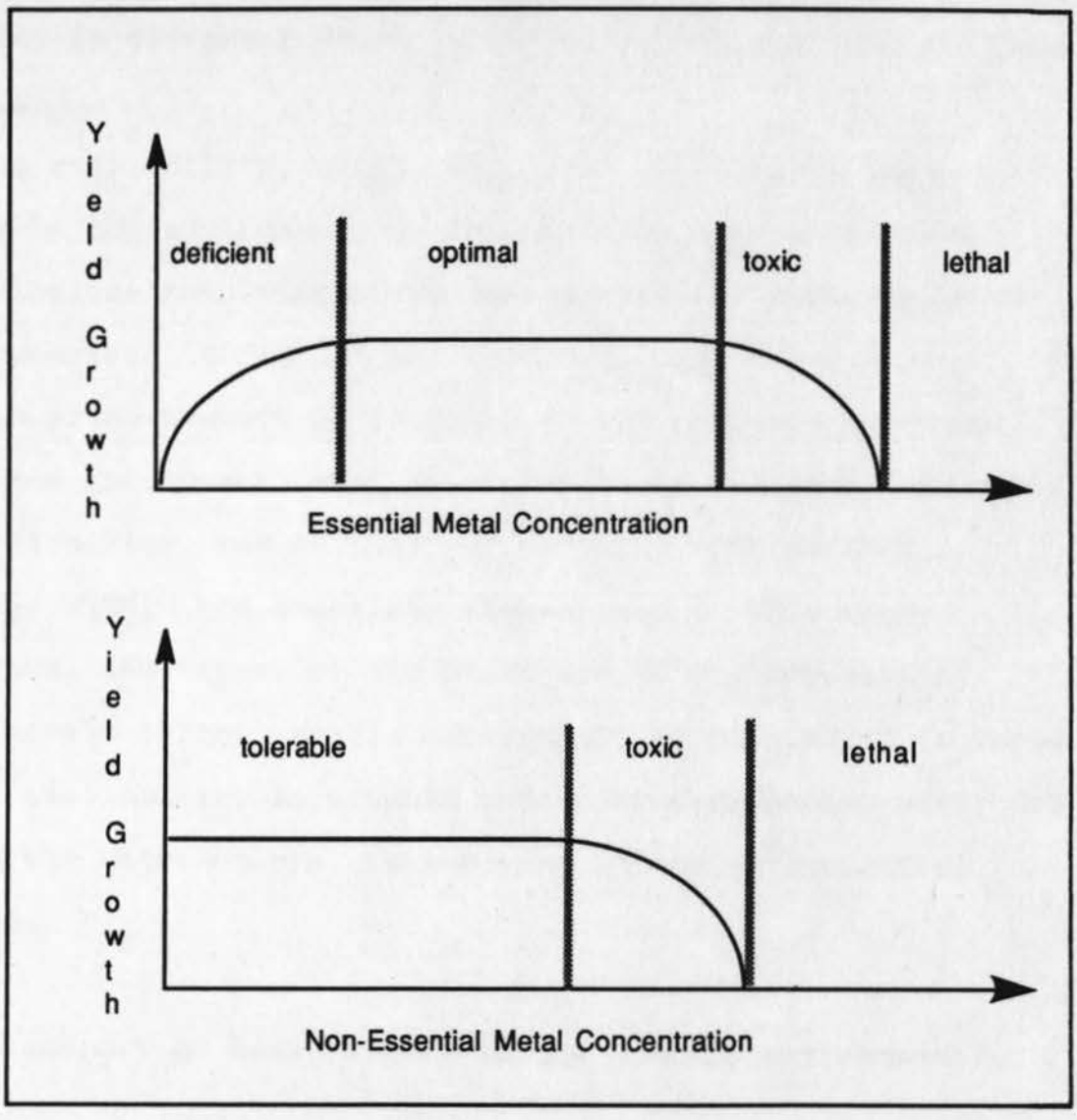
3 = Whether essential (E) to biota

4 = Whether a known pollutant (P)

5 = Woods' category (see above)

The heavy metals can further be subdivided into those which are essential or non-essential to the biosphere. A deficiency of an essential metal can lead to a lack of growth; sufficient leads to optimum growth and an over supply can result in effects on the organism ranging from stunted development to premature mortality (Fig 2.5). Whilst those not having a recognised biological function are classified as non-essential, their function is not absolutely certain.

Fig 2.5 Ecosystem response to metal availability



The toxicity of the various metals depends on many factors, (Table 2.5). These include those factors relating to the properties of the element itself as well as its interaction with organisms. Individual metals betray their toxicity in different ways, Table 2.6 summarises some of these effects.

The availability, uptake and hence toxicity of heavy metals in the environment is dependent on several factors. These include both biotic, as well as abiotic factors, which are summarised in Fig 2.6 and Tables 2.7 and 2.8.

The present study is confined to the sources, transport modes and incorporation of heavy metals in sediments and their bioavailability, rather than any concerns with metabolic pathways within the organisms themselves. In this study, therefore, the impact of the biosphere on the movement of heavy metals in the aquatic environment is considered in terms of its availability as organic matter or sedimenting particles within the water column, rather than in any physiological context.

iii. Transport of heavy metals in the aquatic environment

The transport and fate of heavy metals in aquatic ecosystems is complex due to the difficulty of defining the relative proportions in dissolved and particulate phases, the lack of establishment of equilibrium conditions and the numerous interactions occurring (Salomons & Förstner, 1984).

Table 2.5 Factors affecting the toxicity of heavy metals in solution (after Bryan 1976).

Form of metal in water	inorganic organic	soluble	ion complex ion chelate ion molecule
		particulate	colloidal precipitated adsorbed
Presence of other metals or poisons	joint action no interaction antagonism	more-than-additive additive less-than-additive	
Factors influencing physiology of organisms and possibly form of metal in water	temperature pH dissolved oxygen light salinity		
condition of organism	stage in life history changes in life cycle age and size sex starvation activity additional protection adaptation to metals		
Behavioural response	altered behaviour		

Table 2.6 The effects of the toxicity of heavy metals on biota. From Fergusson (1990) and MAFF (1993).

Metal	Effect
Cd	Competition with Zn in occurrence with certain enzymes. Cd can bind irreversibly with active sites on the enzyme, destroying normal metabolism.
Cu	Essential to the diets of birds and mammals due to its' enzymatic activity. Excess accumulates in the liver
Pb	Pb salts relatively insoluble in water. 90% of Pb taken up by living organisms accumulates in the bone remaining immobile for years. Any disturbance of normal metabolic function can remain undetected. Non-essential, Pb is found throughout the body.
Zn	Essential trace element, found in all cells. Acts as a cofactor of many enzymes. Excess affects children or individual with erratic metabolisms.
Ni	Toxic to cereals and other crops such as French beans.

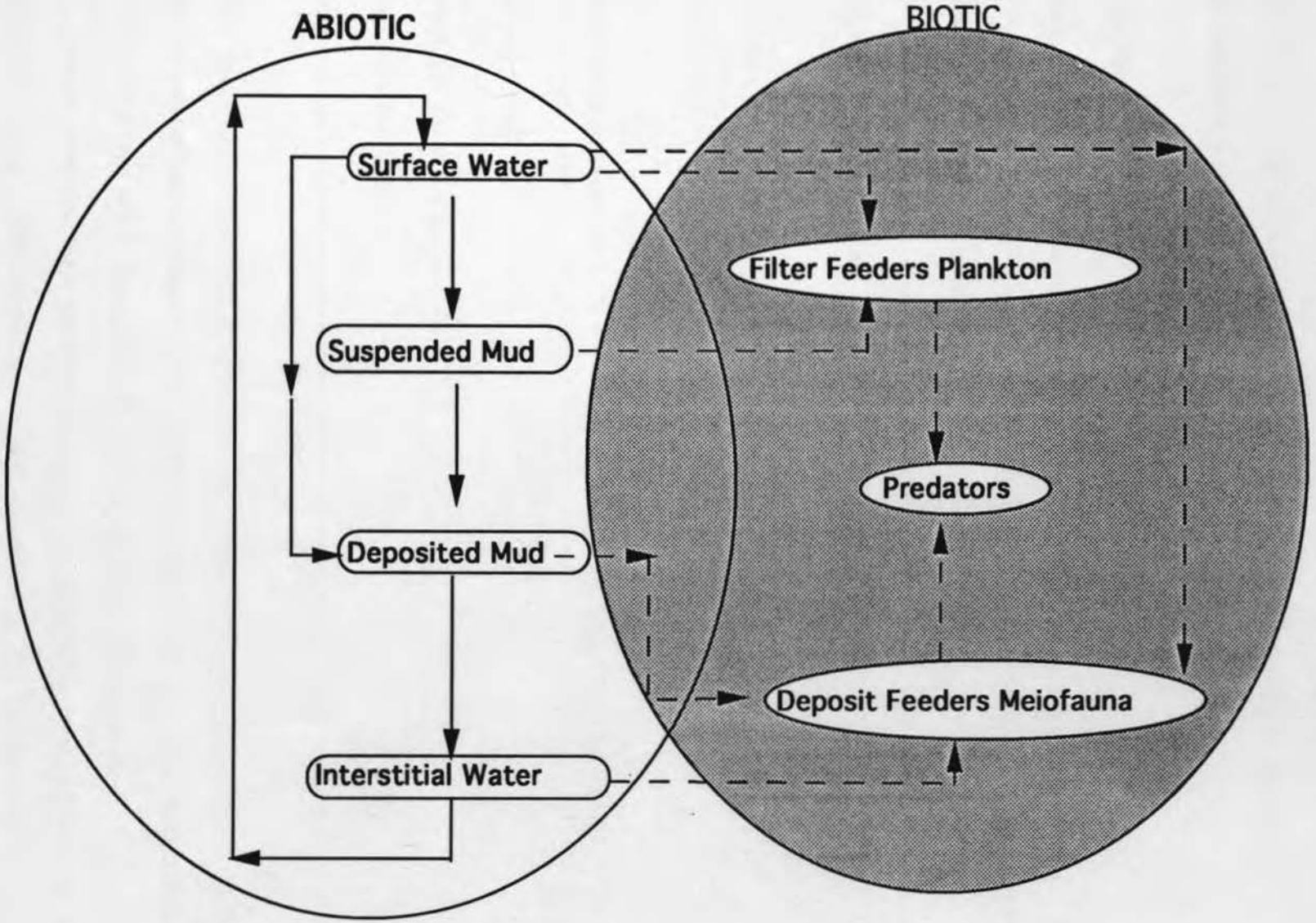


Fig 2.6 Biotic and abiotic factors controlling heavy metal availability in the environment

Table 2.7 Biotic and abiotic factors influencing the availability of heavy metals to the environment. After Fergusson (1990).

Biotic	Abiotic
The life cycle and life history of the organism	Temperature and oxygen content
Seasonal variations	Water hardness
Species specific and individual variability	The presence of organic compounds
Food contamination	The pH of the surrounding medium
Trophic level (in an ecological sense)	

This section outlines the modes of heavy metal transport in the aquatic environment and relates these to a consideration of deposition and speciation in deposited sediment.

Heavy metals can be transported in aqueous solution, as a colloid, or in particulate form. According to Fergusson (1990), this division is arbitrary, being mainly dependent on

Table 2.8 Abiotic factors involved in the availability of heavy metals to the environment. After Fergusson, 1990.

Factor	Effect
Temperature and oxygen content	Influences redox conditions in water and sediment and hence metal availablity. Metal concentrations in interstitial waters associated with anaerobic sediments are 10 times greater than those in supernatant water.
Water hardness	Insoluble carbonates formed, decreasing heavy metal activity. They can then be adsorbed onto calcium carbonate.
Organic compounds	Includes living organisms, organic substrates and synthetic compounds such as PCBs released due to biodegradation. Anthropogenically polluted lakes are commonly eutrophic; the balance between productivity, degradation and incorporation of organic compounds may therefore be disturbed, leading to increased heavy metals.
pH values	Effects of changing pH are indirect as it impacts upon all of the above processes.

particle size. Thus, sizes of 0.45 μm and less are considered to be soluble, sizes greater than 0.45 μm are considered to be either colloidal or particulate, ie in suspension or as sediment respectively.

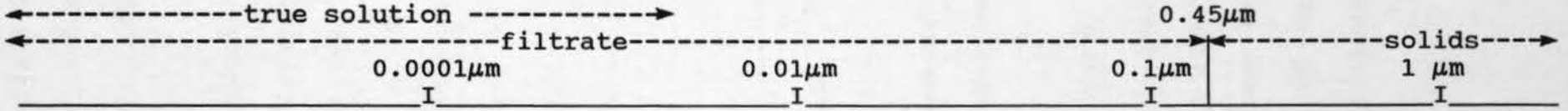
Figure 2.7 illustrates this partition of metals with size, and hence solubility, using Pb and Cd as examples. Figure 2.7 also shows the speciation of heavy metals in water, and the chemical form in which the metal is likely to occur. This depends on several factors including:

1. The solubility, or size, of compounds of the element
2. The oxidation state of the element
3. Whether complexing agents are available
4. Whether complex formation occurs
5. Whether ion-pair formation occurs
6. If particulate material is available, whether adsorption or desorption occurs
7. The nature and availability of biochemical processes

Speciation is important as it fundamentally influences the mobility and toxicity of the metal in the environment (Harrison, 1987). Factor 6 above is particularly important; Förstner & Salomons (1981 a) state that contaminants

"...upon being discharged to surface waters, do not remain solubilised since they are rapidly adsorbed by particulate matter..." Förstner & Salomons (1981 a) p 3

Fig 2.7 Speciation of heavy metals in water dependant on particle size (after Fergusson, 1990)



soluble			colloidal		particulate	
free metal ion	ion-pairs metal chelates	organic complexes	metal species attached to high molecular weight organics	metal species sorbed to colloids	metal species in organic material	inorganic solids, sorption, precipitation
Pb^{2+}	$PbCO_3$ $PbHCO_3$ PbNTA $PbCl^+$	Pb fulvic acid complexes	Pb humic acid complexes	$PbFe(OH)_3$ $PbMnO_2$	Pb amino acids Pb organic complexes	Pb clays $PBCO_3$ $Pb_3(OH)_2(CO_3)_2$
Cd^+	$CdCO_3$ $CdCl^+$ $CdCl_2$	Cd fulvic acid complexes	Cd humic acid complexes	$CdFe(OH)_3$ $CdMnO_2$	Cd amino acids Cd organic complexes	Cd clays $CdCO_3$ (s) CdS

Before adsorption onto particulates, however, heavy metals are transported in a dissolved form in which factor 1 above is of importance. The residence times in a lake give an idea of the rapidity with which heavy metals preferentially adsorb to particulates and are summarised in Table 2.9 for Lakes Michigan and Washington.

Table 2.9 Mean residence times (in years) of heavy metals in lake waters. After Förstner & Wittmann (1981).

Element	Lake Michigan	Lake Washington
Pb	-	5.8×10^{-2}
Cu	8.9×10^{1}	1.3×10^{0}
Zn	3.7×10^{1}	1.8×10^{0}
Cd	4.1×10^{2}	-

Pb has a relatively short residence time, but Cd has a long one reflecting its weaker binding to particles, ie it behaves as a semi-conservative element (Tisue & Fingleton, 1984).

Sigg (1983) demonstrates that the partition between the dissolved and particulate phases is strongly pH dependant. It is likely, therefore, that the transfer of heavy metals from river water to the water column in lakes will not affect

overall chemical conditions; hence leading to little change in speciation. However, as the pH of rainwater varies between 5 and 7 under natural conditions (Petts & Foster, 1985), and possibly as low as 4.5 in areas subjected to 'acid rain', the heavy metals carried in precipitation are likely to be in dissolved form. When they are deposited in a lake, it is likely that large changes in speciation in the top few centimetres of the lake water, sediment or both will result.

It is possible to evaluate the distribution of heavy metals between the dissolved and particulate phases by calculation of partition coefficients:

$$K_D \ (m^3 \ kg^{-1}) = \frac{C_s \ (\text{moles } kg^{-1})}{C_w \ (\text{moles } m^{-3})} \qquad \text{(Equation 2.2)}$$

where:

C_s = concentration in particles

C_w = concentration in soluble form

The coefficients for Zn, Cu, Cd and Pb, valid for Lake Constance, are given in Table 2.10. If the partition coefficient is less than 100 then the amount in solution is 90% of the total. The coefficient for lead is uncertain as its C_s is not really known with any accuracy. It appears to show preference for existing in the particulate phase. A partition coefficient (K_D) of 10^3 indicates that the soluble concentration is 50% of the total. Direct experiments

Table 2.10 Particle-water partition coefficients (K_D) determined from their concentrations in water compared to that of settling particles. After (Sigg, 1983).

	Zn	Cu	Cd	Pb
Water	1-2	0.3-1.0	$5x10^{-3}$-0.02	0.05-1.0
Particles	130	30	0.3	50
Partition Coefficient	100	35	30	1000

with Cd and Cu have confirmed that they preferentially exist in the dissolved phase (Sigg, 1983), although their partition coefficients for Lake Constance indicate that in that environment, with K_Ds of 30 and 35 respectively, it would be expected that 90% of Cd and Cu would be in the dissolved phase. Work carried out by Proffitt (1993) on contaminated river water in the River Sherbourne (English Midlands) shows that partition coefficients can be site or environment-specific. Table 2.11 shows the percentage of individual heavy metals present in water in the particulate phase.

Table 2.11 Average percentage of heavy metals carried in the particulate phase of suspended sediments in rivers in the English Midlands. From Proffitt, 1993, p 49.

Element	percentage in suspended sediment
Zn	45.2
Pb	96.3
Cu	58.78
Ni	65.0
Cd	79.5

The element with the highest proportion transported on particulates is Pb; this is also the element with the highest K_D according to Sigg (1983). Zn has the lowest proportion transported in particulate form in English Midland rivers in contrast to its K_D presented for Lake Constance (Table 2.10), with Cd, Ni, and Cu lying between these two extremes.

a. Speciation of heavy metals in water

The speciation of the heavy elements in water is dependent upon many physical, chemical and biological factors (Brezonik *et al.*, 1991). These are outlined in Table 2.12. These environmental conditions determine the speciation (the chemical form in which the metal occurs) of the heavy metal in

Table 2.12 Environmental conditions affecting the speciation of heavy metals in solution (Brezonik *et al.*, 1991).

Solution conditions

General: Ionic strength (M)) No great variations shown
) in freshwater

Temperature) Seasonal significance

pH
Eh

Specific conditions which relate to binding of the metal to the ligand : generally thought to be available to aquatic organisms

Concentrations and nature of inorganic ligands:
Alkalinity (HCO_3^-, CO_3^{2-})

Presence of anions in anoxic water: F^-, Cl^-, SO_4^{2-}, HS^-

Industrial waste contamination : CN^-

Concentrations and nature of organic chelating agents : generally thought not to be available to aquatic organisms

DOM) Important in
Aquatic humus) bioaccumulation and
Natural organic acids) toxicity especially with regard to complex formation

Peptides) Can be important
Polyaminocarboxylates) complexing agents
) in some surface
) waters

Concentrations and nature of surface sites available on particulate matter for metal binding

Time

An important consideration is the time available for thermodynamic equilibrium to be reached. Reactions involving complex formation on ligands can take time and are dependant on the conditions outlined above.

Reactions involving oxidation and reduction can be slow and can also be dependant on similar conditions to complex formation.

---

solution. The following section briefly discusses the importance of pH and Eh in heavy metal speciation.

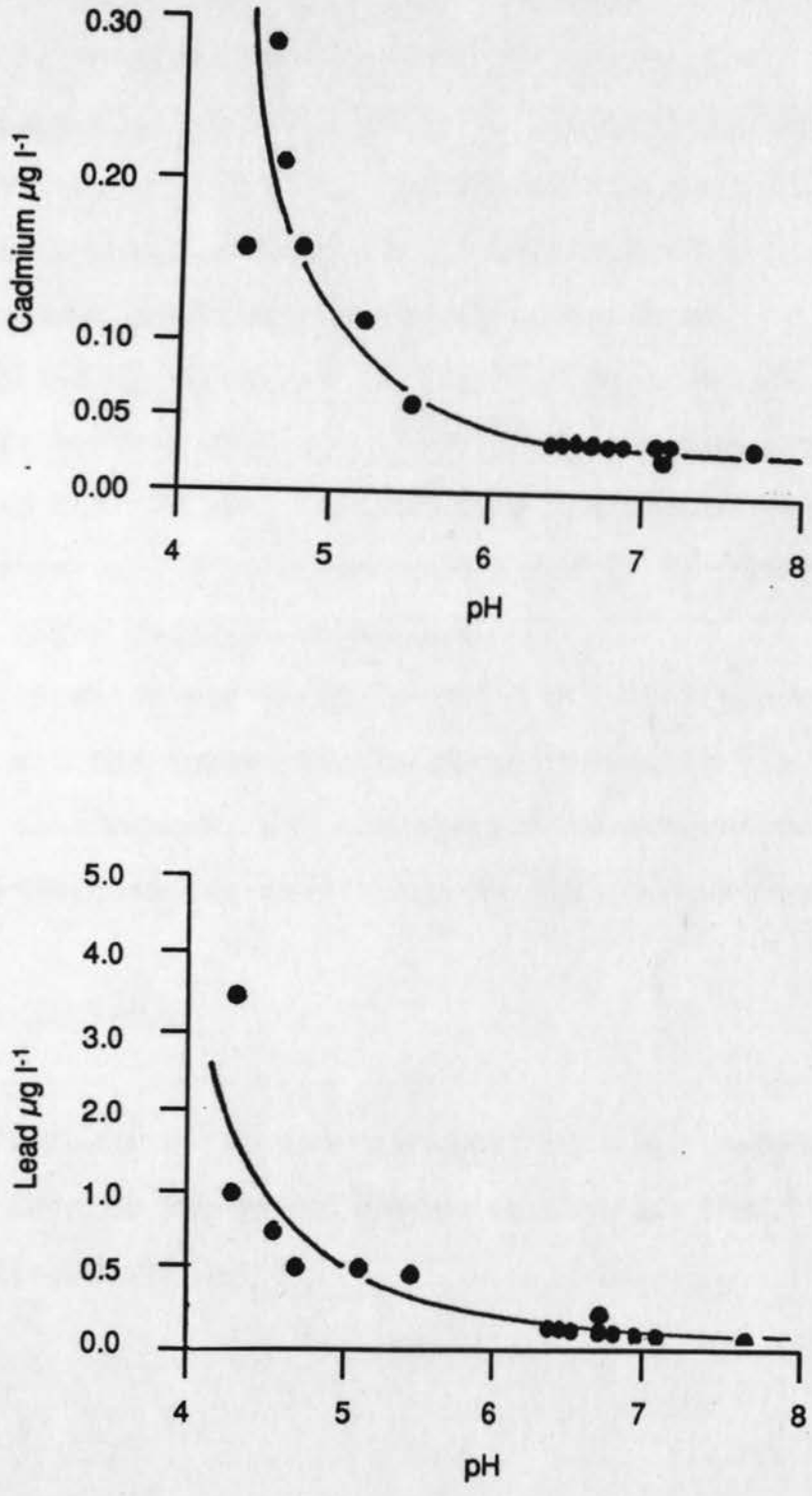
1. pH

Lunt *et al.* (1989) emphasise the importance of pH in determining the speciation of the metal in the dissolved phase. There can be a very abrupt change over a small pH range of 1-2 units. Förstner & Kersten (1988) illustrate the dependence of metal solubility on pH with case studies undertaken by Dickson (1980) from 16 Swedish lakes (Fig 2.8). These graphs show minimum solubilities for Cd and Pb at neutral pHs and increasing solubility with increasing acidity. pH is therefore an important environmental variable to consider from the point of view of remobilisation of heavy metals, particularly should the conditions change due to acid rain or accidental acid spillage within the catchment.

In the natural environment, the range of conditions tolerable to biota is narrow; hence when considering the chemistry of heavy metals in the natural environment it is only necessary to consider a narrow range under normal circumstances.

The normal pH for natural river water lies between 4 and 9 (Petts & Foster, 1985), although accidental spillages of industrial effluent can occur lowering the pH to as little as 2 (Foster *et al.*, 1990).

Fig 2.8 Dissolved metal concentrations ($\mu g\ l^{-1}$) relative to pH in 16 lakes on the west coast of Sweden (after Förstner and Kersten, 1988)



2. Eh

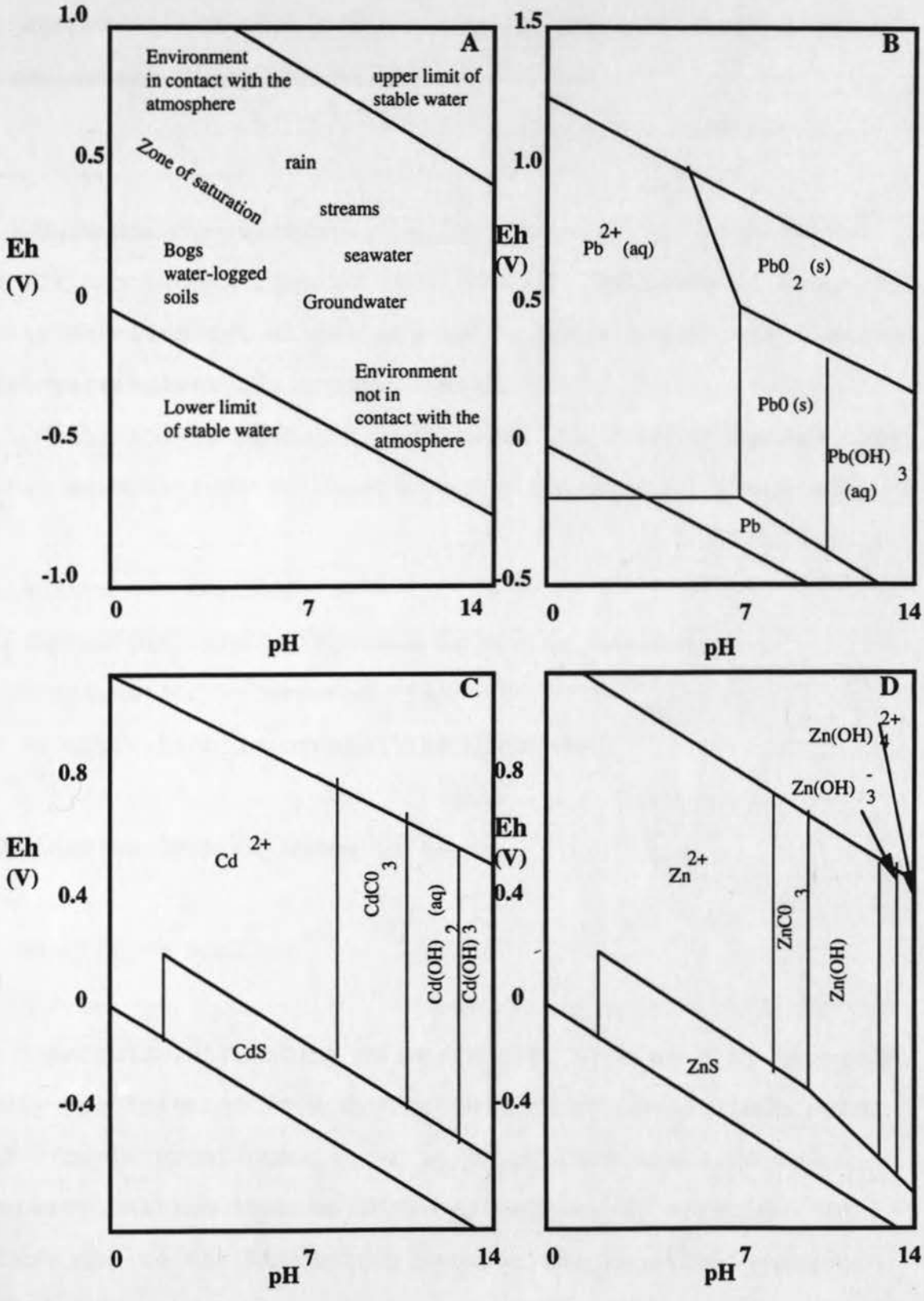
Eh is a measure of redox potential and defines whether the environment is experiencing oxidising or reducing conditions. Fig 2.9a shows the range of Ehs found in the natural environment. Fig 2.9a is also a combined Eh-pH diagram and illustrates the interaction between these two properties. The zone of stable water trends across the centre of the diagram with the zone of the natural environment in the central one third. Taking individual heavy metal elements, the Eh-pH diagrams for Pb, Cd and Zn are shown in Figs 2.9 b, c and d. Cd exists as Cd^{2+} in aqueous solution up to pH 9, whereas Zn^{2+} exists to pH 7.5 and Pb^{2+} to pH 7. The Eh does not affect the form of these elements in stable water except for Zn in which ZnS appears stable under reducing conditions.

The exact form in which the metal is found will influence its bioavailablity and the nature of the interactions of the pollutant with the environment, but its species is determined by the prevailing environmental conditions as outlined above.

b. Transport on particulates

The most important mechanism for the transport of heavy metals and their eventual loss to the water column is through their attachment to settling particles :

Fig 2. 9 Eh / pH diagrams
a. Natural waters (after Petts and Foster, 1985) b. Pb (after Fergusson, 1990)
c. Cd (after Fergusson, 1990) d. Zn (after Förstner and Wittmann, 1981)



" In most aquatic systems, concentrations of trace metals in suspended sediment are far greater than concentrations of trace metals dissolved in the water column."

Horowitz (1985) p 1

This section examines the various ways in which heavy metals can become incorporated into the sediment of lakes by their settling out at the mud-water interface in association with particulate and organic material.

Gibbs (1973) suggests that there are four groups of heavy metal associations in aquatic solid substances. These are:

1. Adsorptive bonding
2. Coprecipitation by hydrous Fe and Mn oxides
3. Complexation by organic minerals
4. Incorporation in crystalline minerals

Considering each of these in turn:

1. Adsorptive bonding

Some materials making up sediments, such as clay minerals, newly precipitated iron hydroxides, amorphous silicic acids and organic substances, have large surface areas. This property enables them to exchange cations by sorption. This occurs due to the attraction between the negatively charged sites on the clay minerals such as $SiOH^-$, $AlOH_2^-$ and $AlOH^-$, or

$FeOH^-$ groups in iron hydroxides or carboxyl and phenolic OH^- groups in organic substances, and the positively charged cations, represented by the individual heavy metal. Preferential adsorption of certain cations occurs which selectively balances the overall charge on the particle. Charges are equalised when an equivalent charge is released from the particle when the heavy metal is adsorbed. All fine-grained sediments are able to attract heavy metal ions at the solid-liquid interface because of intermolecular forces due to their large surface area.

The pH of the environment and the resultant charge on the surface of the particle affects its behaviour as shown in Table 2.13. Hydrous oxide surfaces are used as they have been studied in detail and therefore can be used as models of the particles occurring in natural waters (Sigg, 1987)

Table 2.13 The effect of environmental pH on the surface charge of hydrous oxides

Prevailing environmental conditions	surface charge on particle	type of exchanger
Basic	negative	cation
Acidic	positive	anion

Under basic environmental conditions, a hydrous oxide with negative surface charge would be a cation exchanger and sorb heavy metals to its surface. On the other hand, a hydrous oxide under increasingly acidic conditions is more likely to act as an anion exchanger. It has been demonstrated by Guy & Chakrabarti (1975) that the adsorption capacity of different media at intermediate equilibrium concentrations (C_{eq}) of the individual metal has different properties. The adsorption of Cu, Pb, Cd and Zn onto clay minerals should exhibit no maximum, whereas the adsorption of the same ions onto humic acid and Fe and Mn oxides would exhibit an adsorption maximum. In other words, C_{eq} is reached where the number of cations adsorbed is equal to their concentration in solution. Adsorption onto clay minerals results in increased adsorption with increased concentration. On the other hand, in the case of sorption with Fe and Mn oxides and humic acids, adsorption is finite. Adsorption of heavy metal ions onto clays may therefore not simply involve the binding of the ion to specific sites on the clay. Indeed, it may be that the heavy metal not only replaces cations on the clay particle, but also diffuses into the crystal lattice of the clay in relatively small amounts.

A controlling factor in the sorption of heavy metals to clays may be pH (Förstner & Wittmann, 1981). H^+ competes with the positively charged heavy metal ion for exchange sites. At increasingly acid pH, the heavy metals may be released from

the binding site as they cannot compete with the high concentrations of H^+.

2. Coprecipitation by hydrous Fe and Mn oxides

Fe and Mn oxides and hydroxides occur as mineral coatings and as finely divided particulate material in soils and in the aquatic environment.

These coatings and particles are capable of sorbing or coprecipitating heavy metals (Förstner & Wittmann, 1981). They are, therefore, important sinks of these metals and directly control their distribution within the enviroment. However, the sorbed metal can easily become remobilised should environmental conditions change; more specifically under reducing conditions, whereupon the hydrous Fe and Mn oxides can become a source of heavy metal contamination.

3. Complexation by organic materials

Organic substances in natural ecosystems consist mainly of the remains of biota and their metabolism products and of abiotic, or synthetic, organic materials.

The attachment by complexation onto organic matter by heavy metals is important in that it influences the behaviour of the metal within the aquatic ecosystem. Singer (1977) divided the effects of dissolved organic substances on the behaviour of trace metals into 5 major groups :

a. Complexation of metals with organic matter changes the availability of the metal

b. The distribution of the metal between the oxidised and the reduced form is changed

c. By effectively removing the metal from the water column, the organic matter-trace metal complex reduces the toxicity of the metal by essentially removing it from the water column and hence from close proximity to biota.

d. The extent to which metals are subsequently adsorbed onto suspended sediment is directly affected by dissolved organic material

e. Colloid containing metals are less stable in the presence of such organic matter.

Once formed, the complex can then either be adsorbed onto particulate sedimentary material for incorporation into the bed sediment of the lake, or it can precipitate directly onto the sediment itself.

4. Incorporation in crystalline minerals

Heavy metals may be located in the lattices of minerals; their incorporation is dependent upon ionic radii, valencies and

electronic configuration. The bonding generally occurs in inert positions in the crystal lattice and, once incorporated, the metal may be considered unavailable to the environment.

Whilst it is possible to theorise about these binding sites in isolation, in practise many interactions between the different sites occur in natural situations, eg there is strong evidence to suggest that particulate matter has a thin covering of natural organics (Hart, 1982) which would influence the binding of heavy metals to particulate matter.

2.6 Selection of heavy metals in the research programme.

The elements chosen for this study (Cd, Ni, Cu, Pb and Zn) were selected for 6 main reasons:

1. They have known pollutant properties

2. They are classified in the third of Woods' three categories, as outlined in Section 2.3i, ie that they are toxic and readily accessible to the environment.

3. Each element is frequently used in consumption and production related processes and hence is commonly found in the urban environment (Tables 2.2 and 2.3).

Pb is the most widely used heavy element industrially (Fergusson, 1990) and, with Cd, is of concern to health. The use of Ni and Cd in battery production is increasing, as is Zn

in the electroplating industry. Cu has been widely used in many processes including the manufacture of electrical cables and in coinage. The use of a Zn : Pb ratio as an index of production (of Zn in, for example, the electroplating industry) versus consumption (of Pb in leaded fuel) has been used by Foster *et al.*, 1994, and appears to show a relative decrease with increasing urbanisation. This ratio will be examined in Chapter 7.

4. Cu, Cd, Pb, Ni and Zn have been widely used in research carried out to assess the extent of heavy metal pollution and information derived from this study would therefore provide comparative data.

5. The five elements chosen are readily analysed using standard acid digestion techniques followed by analysis using atomic absorption spectrophotometry.

6. The elements chosen are readily transferred to the sediment at the mud-water interface. Mobility of heavy metals across the mud-water interface can be viewed as an 'equilibrium' in which the balance is in favour of transfer to the sediments (Jennett *et al.*, 1980).

Mobility of the elements, once incorporated in the sediment, could be a problem in that it could change the

distribution of the metal within the sediment profile. In the case of within-sediment mobility, Alderton (1985) states that :

"Mobilisation of metals and organic compounds within the sediment is assumed to be of minor importance in most instances."

Alderton (1985) p 1

Farmer *et al.* (1980), found no evidence for diagenetic mobility of Pb, Zn, or Cd in the sediments from Loch Lomond, but did find evidence of mobility of As in that 80% of the total excess for As was found in the upper 4 cm of the core.

The five elements chosen appear to conform to Alderton's (1985) prerequisites for a pollutant to provide a historical record of enrichment; they have an affinity for the sediment, and do not remain preferentially in the dissolved phase an observation generally supported by the research on contaminated Midland rivers given in Table 2.11, except for Zn.

2.7 Choice of field sites.

As pointed out by Macklin (1992), the heavy metal content of urban soils has been largely ignored in recent research, particularly when consideration is given to the large body of work concerned with agricultural soils in Britain. The same is true of urban lakes, in which very little work has been carried out on the pollution status of inner city lakes and

pools in the UK. Whereas problems exist in assessing background concentrations in urban soils due to overprinting by metal contaminants from, for example, vehicle exhaust emmissions, this is not the case when analysing a lake core which represents the gradually accumulated results of historical contamination.

The first site chosen for the present study, Swanswell Pool, is a city centre site (Fig 3.6) which has been a closed basin for the last 150 years (section 3.4.1). It provides some degree of experimental control in that it receives contributions mainly from the atmosphere.

The second site, Wyken Slough, comprises the Slough, an area of marshland and a lake, Wyken Pool itself. It is fed by two inflowing streams, and has a catchment with various sources of pollution. Characteristics of both pools are given in Table 2.14 and further detailed descriptions of both sites are given in Chapter 3.

Section 2.4 outlined the numerous studies undertaken in areas of mining and the effects of the urbanised area at some distance from the source of contamination. However, there has been no assessment of the gradient of atmospheric pollution from the urban area into rural regions using lake sediments. Work complementary to this type of study has been carried out in the Geography Department, Coventry University in two other regions of the UK:

1. Rural locations in North Warwickshire in close proximity to, and downwind of, Midland England industrial conurbations but with no direct catchment sources of metal

Table 2.14 The characteristics of Swanswell Pool and Wyken Slough

	Swanswell Pool	Wyken Slough
Grid reference	SP335795	SP363833
Resevoir area (ha)	0.73	2.25
Catchment area (ha)	220.0*	450.0
Resevoir:catchment	1:301*	1:200
Max. altitude (m)	105*	112
Mean water level (m)	70	85
Relative relief (m)	35	27
Max. depth (m)	1.3	0.8
Mean depth	0.9	0.6
Volume (m^3)	6389	13050
Date impounded	1265	c.1850
Present land use % area		
Urban	100	c. 40
Permanent pasture	0	c. 60

* by the twentieth century, the catchment area was reduced to < 1 ha. The inflowing streams were culverted in 1850 and the hospital spring feeders were cut off in the 1960's (Chapter 3.4.1 and Table 3.2). The reservoir : catchment ratio was reduced to c. 1 and the catchment altitude reduced to < 2 m above mean water level.

contamination. The two sites are Seeswood Pool and Merevale Lake, with predominantly agricultural and forested catchments respectively. Catchment descriptions are given elsewhere (Foster *et al.*, 1987a and 1991), but the major source of heavy metals to these lakes is from the atmosphere (Foster *et al.*, 1991).

2. Isolated lakes and reservoirs remote from local and regional sources of atmospheric pollution and with no direct catchment derived sources of contamination. (Foster, 1987; Dearing *et al.*, 1989). The two sites are Porth Hellick and Big Pool, Isles of Scilly. Catchment descriptions for these lakes are given elsewhere (Foster *et al.*, 1991), but Big Pool, like Swanswell Pool has no channelled inflow, and for both sites the only source of heavy metals is from the atmosphere.

The data from the current study will be set in the context of findings from the investigations outlined above.

2.8 Sampling strategies.

This section justifies the sampling strategy employed at both sites. As Swanswell Pool has effectively no catchment, sampling concentrated on the lake sediments and on water quality. However, in the case of Wyken Slough, the catchment components are considered individually. Tables 2.15 and 2.16 summarise the sampling strategy employed at each site. Appendix 2 summarises the field handling of the samples and techniques used for analysis.

Table 2.15 Numbers of lake sediment cores and surface samples taken from each site

a.) Swanswell Pool

12 surface samples

12 Mackereth cores sliced at 1 cm intervals:

	Number of samples per core	depth to red clay
M1	72	--
M2	79	78
M3*	84	48
M4	50	--
M5	55	--
M6*	67	45
M7	55	48
M8*	55	34
M9	70	26
M10*	47	31
M11	56	36
M12	33	31

* cores analysed for heavy metals

Table 2.15 (continued)

b.) Wyken Pool

16 surface samples

16 Mackereth cores sliced at 1 cm intervals

	Number of samples per core	depth to relict soil
AO*	70	61
A1	55	36
A2	73	56
A3	50	40
BO*	77	65
B1	48	30
B2	27	20
B3	48	27
CO*	72	61
C1	75	70
C2	45	37
C3	46	40
DO*	61	51
D1	91	80
D2	50	40
D3	38	30

* cores analysed for heavy metals

Table 2.16 Cores and samples taken from Wyken Slough

Marsh	2 Russian cores sliced at 2 cm intervals
	Core 1 29 samples
	Core 2 24 samples
	20 surface samples
Streams	
Eastern stream	21 bed sediment samples
Western stream	10 bed sediment samples
Bayton Road	5 bed sediment samples
Toxic Tip	6 bed sediment samples
Outlet	1 bed sediment sample
Soils	2 hand gouge cores sliced at 5 cm intervals
	Core 1 10 samples
	Core 2 10 samples

i. Lake sediment

A sample of sediment from the bed of a lake represents only a part of the material deposited there (Feltz, 1980). It is therefore necessary to remove sufficient material for the samples to be representative of the body of sediment as a whole. Multiple cores were taken in this study since analysis of a single core may yield only limited information, indicating rates of accumulation at a single point in the lake

basin. A sampling strategy based on a single core would therefore take no account of the differences in spatial loadings of contaminants across the bed of the lake as a whole (Foster *et al.*, 1987b).

Dearing (1986) points out the difficulties of accurately locating sampling sites when coring in open water from a boat. This effectively precludes random sampling and for this reason both Swanswell Pool and Wyken Pool were cored on a systematic grid system (Figs 2.10a and 2.10b.)

Dearing (1986) and Foster *et al.* (1990) have reviewed previous lake studies and their coring densities. The data are reproduced in Table 2.17 including those of Swanswell Pool and Wyken Pool. Whilst there is no recommended optimum coring density, the framework adopted at the two Pools compares favourably with other multiple cored sites.

As Dearing (1986) points out, sampling density depends on physical parameters such as lake area and the irregularity of sedimentation as well as the time and finances available and the amount of energy required to carry out the project. The strategy employed at Swanswell Pool and Wyken Slough was designed with these criteria in mind as well as that of representativeness.

In the case of Swanswell Pool, N-S and W-E transects were established by siting ranging poles along the dam wall and the eastern side of the pool at regular 30 m intervals (Fig 2.10a). A rope was attached to either the dam wall or fountain outlets and an anchor used to steady the boat between the two fixed ropes; any slack being taken up on the ropes so they were kept taut.

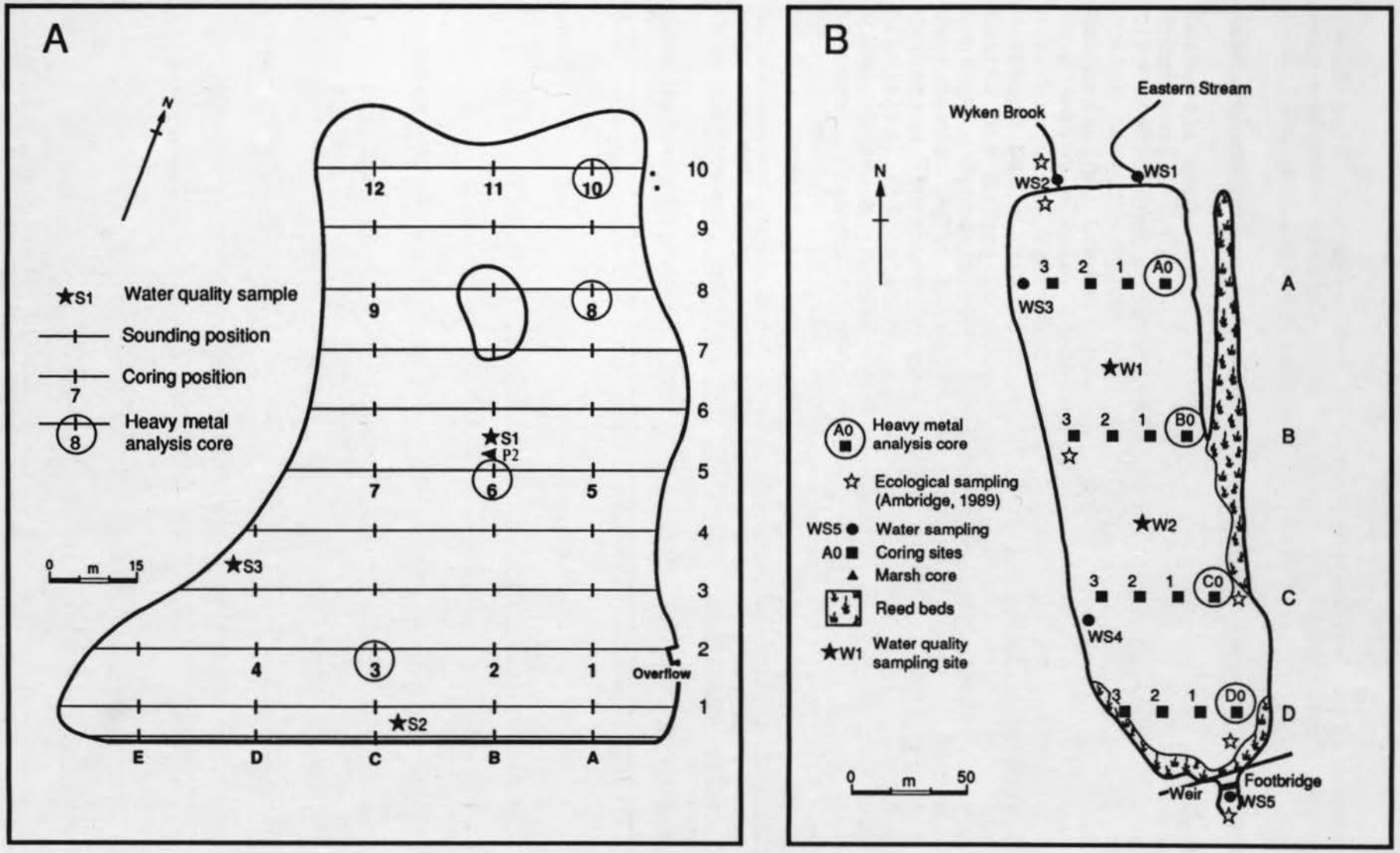


Fig 2.10 Sampling strategies at
a. Swanswell Pool
b. Wyken Pool

Table 2.17. A comparison of coring densities of published lake sediment studies with those of Swanswell Pool and Wyken Pool (Updated from Foster *et al.*, 1990)

Site and author	Number of hectares per core
Swanswell Pool	0.06 ha^{-1}
Wyken Pool	0.14 ha^{-1}
Llyn Goddionduon,N.Wales (Bloemendal *et al.*, 1979)	0.04 ha^{-1}
Frains Lake, Michigan (Davis, 1976)	0.3 ha^{-1}
Havgårdssjön, Sweden (Dearing, 1986)	1.0 ha^{-1}
Llyn Peris, N Wales (Dearing *et al.*, 1981)	1.3 ha^{-1}
Merevale Lake, Warwickshire,UK (Foster *et al.*, 1985)	0.08 ha^{-1}
Seeswood Pool, Warwickshire,UK (Foster *et al.*, 1986a)	0.16 ha^{-1}
Egari, New Guinea (Oldfield *et al.*, 1985)	1.7 ha^{-1}
Loe Pool, Cornwall, UK (O'Sullivan *et al.*, 1982)	1.0 ha^{-1}
Geirionydd, North Wales (Foster *et al.*, 1990)	0.87 ha^{-1}
Catherine, Northern Ireland (Foster *et al.*, 1990)	1.5 ha^{-1}
Llangorse, Mid Wales (Foster *et al.*, 1990)	3.0 ha^{-1}
Roumi, Morocco (Flower *et al.*, 1989)	12.1 ha^{-1}
Affougah, Morocco (Flower *et al.*, 1989)	1.2 ha^{-1}
Azigza, Morocco (Flower *et al.*, 1989)	7.4 ha^{-1}
Bussjo, Scania, Sweden (Foster *et al.*, 1990)	0.12 ha^{-1}
Lake Geneva, Switzerland (Krishnaswami *et al.*, 1971)	one core
Lake Windermere, English Lake District (Hamilton-Taylor, 1979)	two cores
Lake Monona, Wisconsin, USA (Bortleson and Lee, 1974)	two cores

Ranging poles were also set up along the inlet end and western edge at Wyken Pool at 62.5 m intervals (Fig 2.10b). As there was no means of tying the boat off, an anchor was deployed and the boat allowed to drift into position with the prevailing wind.

ii. Marsh

There is evidence to suggest that plants can selectively take up heavy metals in their tissues and hence effectively remove the metal from the environment; this is true of terrestrial plants (Baker *et al.*, 1990; M^{c} Grath *et al.*, 1993 a and b) and those growing in wetlands (Harding & Whitton, 1978; Glooschenko *et al.*, 1981; Gambrell *et al.*, 1982; Ajmal *et al.*, 1988). Marsh plants have been used in the water purification process (Lee *et al.*, 1976; Gambrell *et al.*, 1977; Green, 1993; Upton et al., 1994) and, in the case of soils, it may become economically viable to recover the metals which are assimilated systemically (Baker *et al.*, 1990; M^{c} Grath *et al.*, 1993 a and b). Preliminary work at Wyken Slough marsh by Ambridge (1989) indicated that it selectively accumulated heavy metals from the environment and concentrated them in roots and stems of living vegetation. Any study of the reconstruction of the history of this site must therefore consider the action of such sinks as they affect the amount of metals ultimately delivered to the lake.

The marsh at Wyken Slough is associated with the Eastern stream (Fig 2.10 b) and was cored on a systematic grid system (Fig 2.11 a) using a hand gouge (Fig 2.12). Bulked

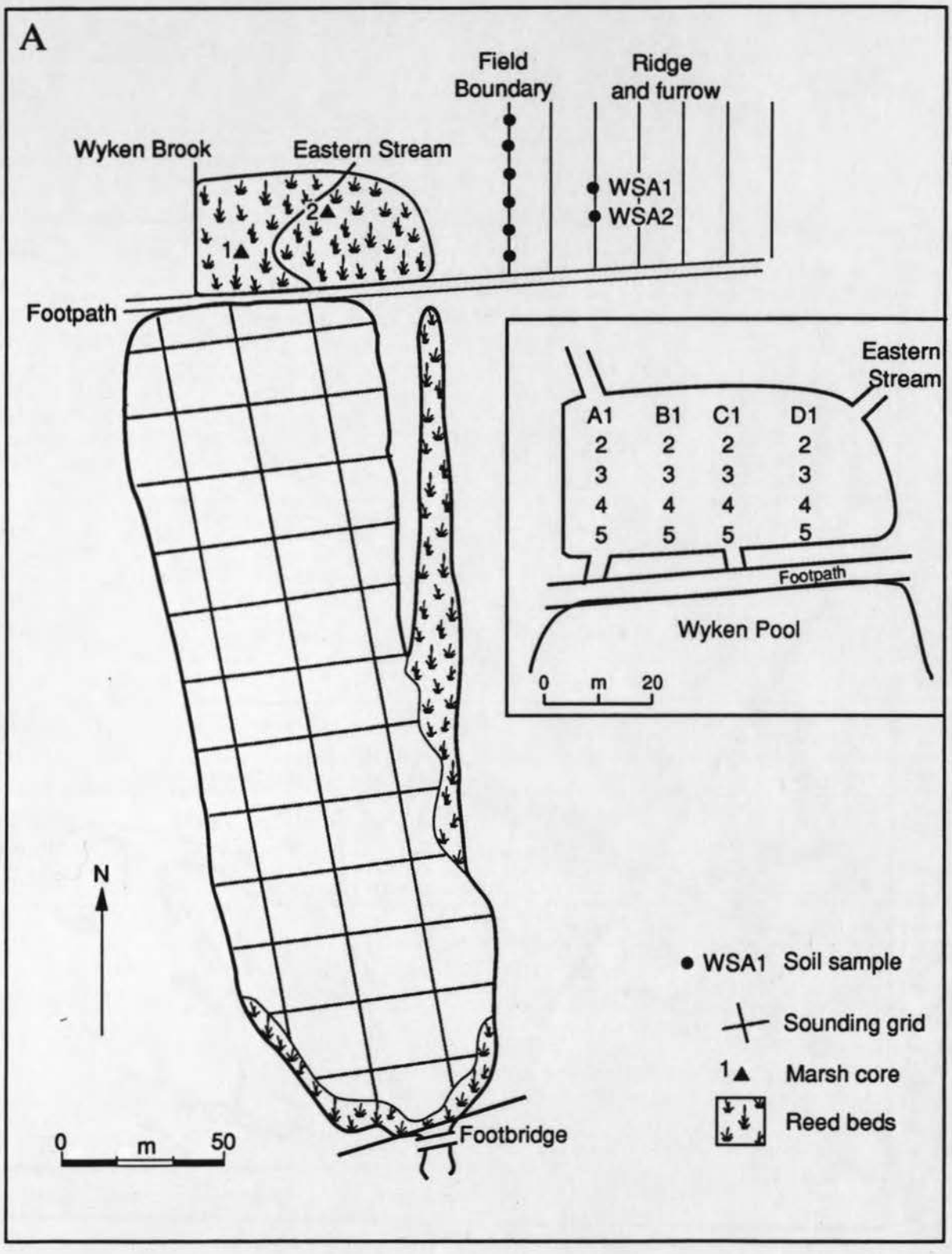
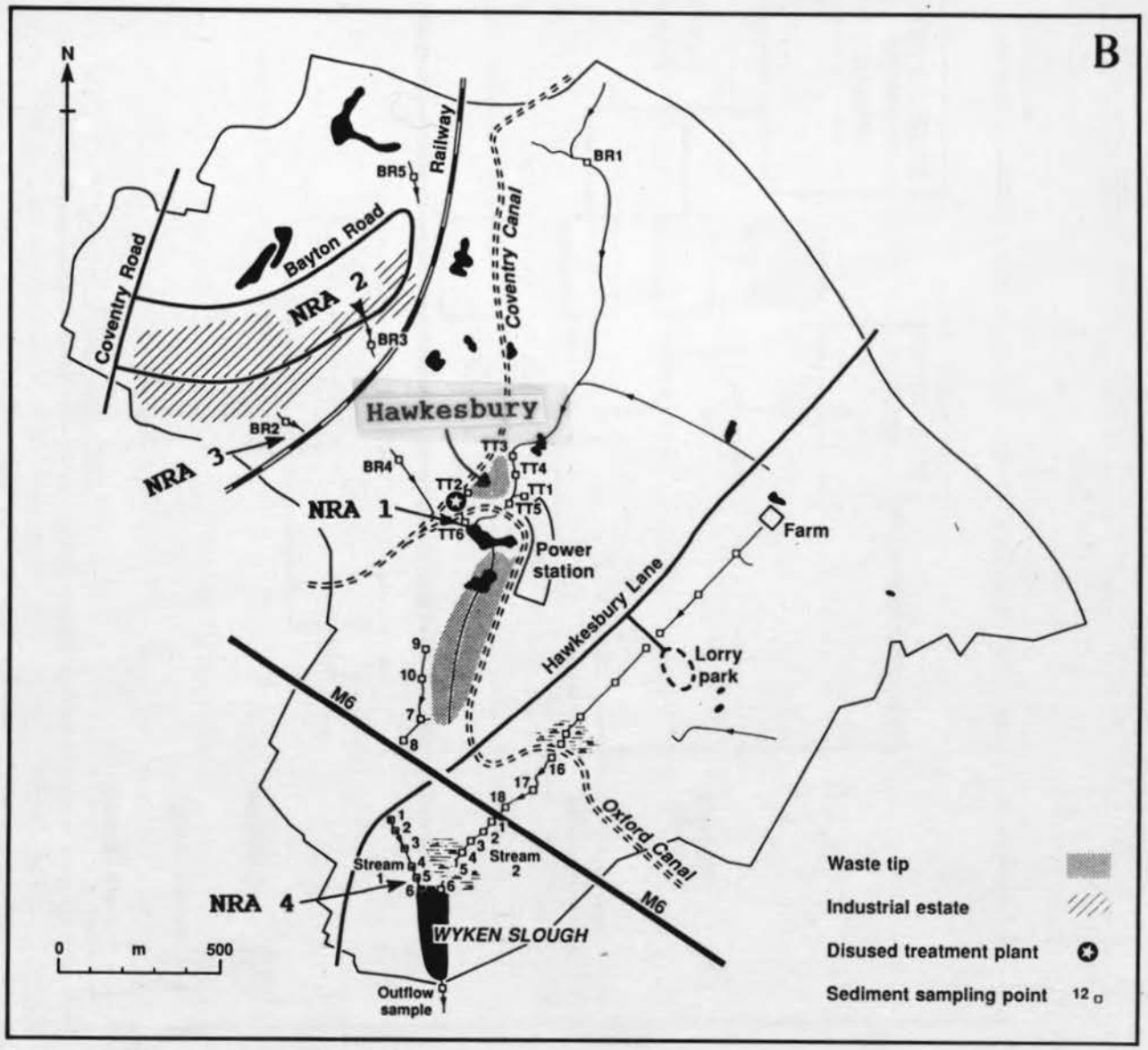
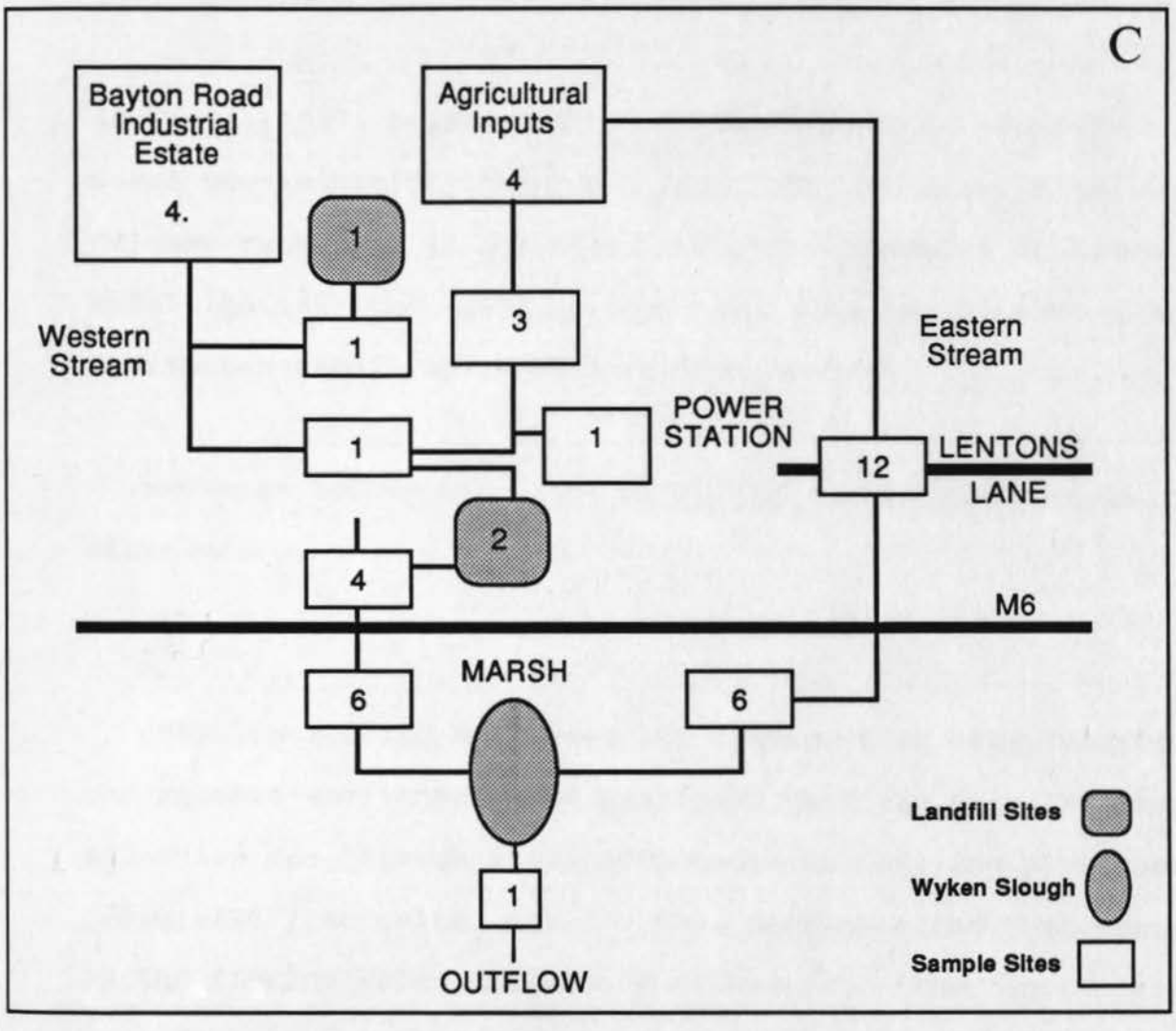


Fig 2.11 Sampling strategies at Wyken Slough
a. Marsh samples
b. The Wyken Slough catchment
c. Schematic diagram of stream bed sampling sites



(NRA = sampling sites for water quality undertaken by the NRA (Severn Trent Region)


C
Bayton Road Industrial Estate
4.
Agricultural Inputs
4
1
3
Western Stream
1
Eastern Stream
1
1
POWER STATION
12
LENTONS LANE
2
4
M6
MARSH
6
6
1
OUTFLOW
Landfill Sites
Wyken Slough
Sample Sites

samples of the top 10 cm of the core were taken for analysis. Two 1 m Russian cores (Fig 2.12) were also taken from the marsh at the sites marked on Fig 2.11 a to assess the vertical distribution of heavy metals in the marsh. The grid was set out using ranging rods set at 10 m intervals and plotting the crossing points by means of measuring tapes.

iii. Streams

As Thoms (1987) points out, there have been few studies of metal contamination in urban rivers, particularly in the UK. Streams represent an important means of transport of heavy metals through the aquatic ecosystem. They can receive urban stormwater runoff which Ellis (1976) states

"..may well become the major degrading factor in receiving streams."

Ellis (1976) p 730

Section 2.5iiib discussed the transport of heavy metals in the aquatic environment and concluded that the most important mechanism was through their attachment to settling particles (Sigg, 1987; Horowitz, 1991). These particles are transported in the flowing water until they settle out either on the river bed, in a lake or they can be lost to the freshwater part of the hydrological cycle and subsequently deposited in an estuary or out at sea. Urban stream water and sediments should therefore be integrated into any study of catchment response to increased urbanisation and industrialisation.

As outlined in section 2.2, however, river or stream sediments do not retain a historical record of heavy metal pollution. They do, however, act as sinks of pollutants both in the short and long term. This is illustrated with particular reference to the effects of mining (Wolfenden & Lewin, 1978; Brook & Moore, 1988) where river sediments retain the evidence of anthropogenic excess pollutants long after the cessation of mining activity. In the case of urban streams, the concentration of heavy metals contained in the channel substrate can form the basis of an assessment of the amount which may become available to the environment should conditions change.

Samples of bed sediment from inflowing streams at Wyken Slough were taken from sites where access could be gained to surface streams. Much of the stream system flows underground or enclosed in culverts and in many cases the banks have been steeply excavated making sampling hazardous. Fig 2.11 b shows the sampling sites. In order to simplify the interpretation of these data, samples were grouped together on the basis of discrete river reaches, which are represented schematically in Fig 2.11 c.

iv. Soils

As suggested in section 2.2, soils do not lend themselves to an elucidation of the pollution record of an area due to the long industrial history of the UK and consequent overprinting by successive metal contaminants (Macklin, 1988). This overprinting makes it difficult to distinguish between

contemporary and historical contamination events. However, as Table 2.18 shows, the residence times of heavy metals in soils and alluvial deposits is comparatively long (Macklin, 1992) and they therefore represent an important sink of atmospheric wet and dry deposition as well as land-based point sources.

Table 2.18 Residence time (years) of heavy metals in soils and alluvial deposits (from Macklin, 1992)

Cd	75 - 380
Hg	500 - 1000
Pb and Zn	1000 - 3000

It is important to take account of the amount of heavy metals in catchment soils for two reasons:

1. The soil acts as an important sink of heavy metals in the environment

2. The soil acts as an important source of heavy metals. This can occur due to simple erosion whereby the soil particles carrying the heavy metals are removed and transported into the fluvial system, or eroded by wind and moved in the atmosphere. This will have two effects: either the catchment soils are heavily contaminated and the pollution signal will be enhanced wherever the soil is eventually deposited, or the soil is

relatively uncontaminated and the pollution signal will be diluted.

v. Water quality

Assessment of water quality was carried out at both Swanswell and Wyken Pools. This took the form of primary and secondary data by means of direct analysis and analysis of data provided by the NRA (Severn Trent region) respectively (Table 2.19 lists the analyses undertaken at Swanswell and Wyken Pools). As outlined in iii above, urban streams are in receipt of excess heavy metals from a variety of sources. Depending on environmental conditions, these are transported in solution or preferentially sorbed to particles settling out of the water column (Sigg, 1987; Horowitz, 1991). Analysis of the conditions prevailing in the water column at both sites would allow the development of four lines of enquiry:

a. The prevailing environmental conditions would be monitored. Wyken Pool inlets and outlet were monitored at monthly intervals for a year. In addition to the collection of primary data at this site, NRA (Severn Trent region) analyses of both the Pool, and sites within the catchment (Fig 2.11 b) were also used. Water quality sampling sites at Wyken Pool were based on an earlier study undertaken by Ambridge (1989) and were chosen to maintain continuity. The sampling sites are shown on Fig 2.10 b, one sample was taken by each inlet, one from below the outlet and one at each end of the lake.

Table 2.19 Summary of water quality data obtained for Swanswell and Wyken Pools

	1	2	3	4	5	6	7
pH	+	+	+	+	+	+	+
O (mg l^{-1})	+	-	-	+	-	-	-
O (%)	+	-	-	+	-	-	-
BOD + ATU	-	-	+	-	-	+	-
Temperature	+	-	-	+	-	-	+
Eh	+	-	-	+	-	-	+
Conductance	-	+	-	-	+	+	+
Ca	-	+	-	-	+	-	+
Mg	-	+	-	-	+	-	+
Na	-	+	-	-	+	-	+
K	-	+	-	-	+	-	+
NH_4	-	+	-	-	+	-	+
NO_3	-	+	-	-	+	-	+
NO_2	-	+	-	-	+	-	+
SO_4	-	+	-	-	+	-	+
HCO_3	-	+	-	-	+	-	+
Cl	-	+	+	-	+	+	+
PO_4	-	+	-	-	+	-	+
Si	-	+	-	-	+	-	+
TON[1]	-	-	-	-	-	+	-
SS[2]	-	-	-	-	-	+	+
NH_4 -N[3]	-	-	-	-	-	+	-
Zn[4]	-	-	-	-	-	+	+
Cu[4]	-	-	-	-	-	+	+
Ni[4]	-	-	-	-	-	+	+
Pb[4]	-	-	-	-	-	+	+
Cd[4]	-	-	-	-	-	+	+

[1] Total oxidised nitrogen
[2] Suspended solids
[3] Ammoniacal nitrogen
[4] Total and in filtrate for 1 - 6, total dissolved metal for 7.

1. Swanswell Pool, February, 1988, 1 sample at 3 depths in the water column
2. Swanswell Pool, April, 1988, 3 samples
3. Swanswell Pool, NRA (Severn Trent region) water quality data, 1 sample
4. Wyken Pool, January 1988, 2 samples at 3 depths in the water column
5. Wyken Pool, April 1990, 5 samples
6. Wyken Pool, NRA (Severn Trent region), water quality data, 4 samples
7. Wyken Pool water quality sampling, October 1990 to September 1991, 5 samples per month.

Location sites for water quality samples on Figs 2.10 a (Swanswell Pool) and b (Wyken Pool).

Swanswell Pool relies on mains water for its water supply, has no natural inlets or outlets, therefore inlet water quality should change little and it was felt the time should be spent monitoring Wyken Pool rather than Swanswell. The NRA (Severn Trent region) data and water samples taken 3 months apart in February and April, 1988, were used for certain analyses, these are shown on Table 2.19. Measurements were taken at one site in February 1988, but at three depths in the water column to ascertain whether water quality parameters changed with depth. A more detailed chemical analysis was carried out in April 1988 at three sites to include the site analysed in February, one adjacent to the hospital overflow and one adjacent to the public water supply (Fig 2.9a).

b. The stability of sinks of heavy metals could be assessed and hence their availability should environmental conditions change. In section 2.5 iii a) it was suggested that pH was one of the most important controlling variables in the speciation of heavy metals in water. Temperature, total conductivity (a measure of the total ion concentration in solution, Foster *et al.*, 1981) and pH were therefore measured using ELE Paqualab water quality testing probes, to give an indication of prevailing environmental conditions which would be used to assess the stability of the sinks of heavy metals in the sediment column.

c. Any seasonal control on the transport and deposition of heavy metals could be assessed. Sigg (1983) suggests that the deposition of heavy metals may be seasonal as there are more

settling particles in the summer due to greater biotic activity and therefore incorporation of heavy metals may be greater in the summer than in the winter. This may lead to greater loss of heavy metals through the outflow in winter than in summer due to the lower concentration of particles. Higher productivity and higher sedimentation rates in the summer may more effectively remove the heavy metals from the water column, especially Cu and Zn (Sigg, 1983). Since continuous monitoring was only carried out at Wyken Pool, this aspect of water quality sampling is only considered for this site.

d. Förstner & Wittmann (1981) and Förstner & Kersten (1988) suggest that elevated salt concentrations can lead to the release of heavy metals from sediments. Monitoring of Na, Mg, Ca and K, which compete for sorption sites on solid surfaces, may give an indication of the potential for elevated dissolved metal concentrations due to increased loadings of salt washed off roads and delivered to the fluvial systems by storm sewers.

Table 2.20 summarises the water quality analyses undertaken at both sites and justifies their choice. The next section discusses the framework of sample collection.

2.9 Sample collection

Collection of vertical sections of lake sediment involves the removal of cores. Coring devices are generally of two types;

Table 2.20 Justification for water quality analyses undertaken

pH	Relates to the stability of sinks of heavy metals. At acid pH, H^+ competes with heavy metals for binding sites leading to metal release. Eh is a measure of redox conditions, at low Eh, metals are released. Increasing temperature leads to increasing toxicity. Conductivity indicates fluctuations in total ion concentrations.
Eh	
Temperature	
Conductivity	
PO_4 NO_3 NO_2 Si NH_4 SS	Relates to falling particles, gives an indication of productivity and whether eutrophication may be a problem (SS = suspended sediment)
Cl Na Mg K Ca	Relates to the competition between salts and heavy metals for binding sites. High concentrations of salts can lead to release of heavy metals.
Zn Cu Cd Pb Ni	Concentration of heavy metals carried in solution

See also Tables 2.7, 2.8, 2.12

end filling and side filling (Moore & Webb, 1978; Lowe & Walker, 1984; Aaby & Digerfeldt, 1986; Faegri & Iverson, 1989).

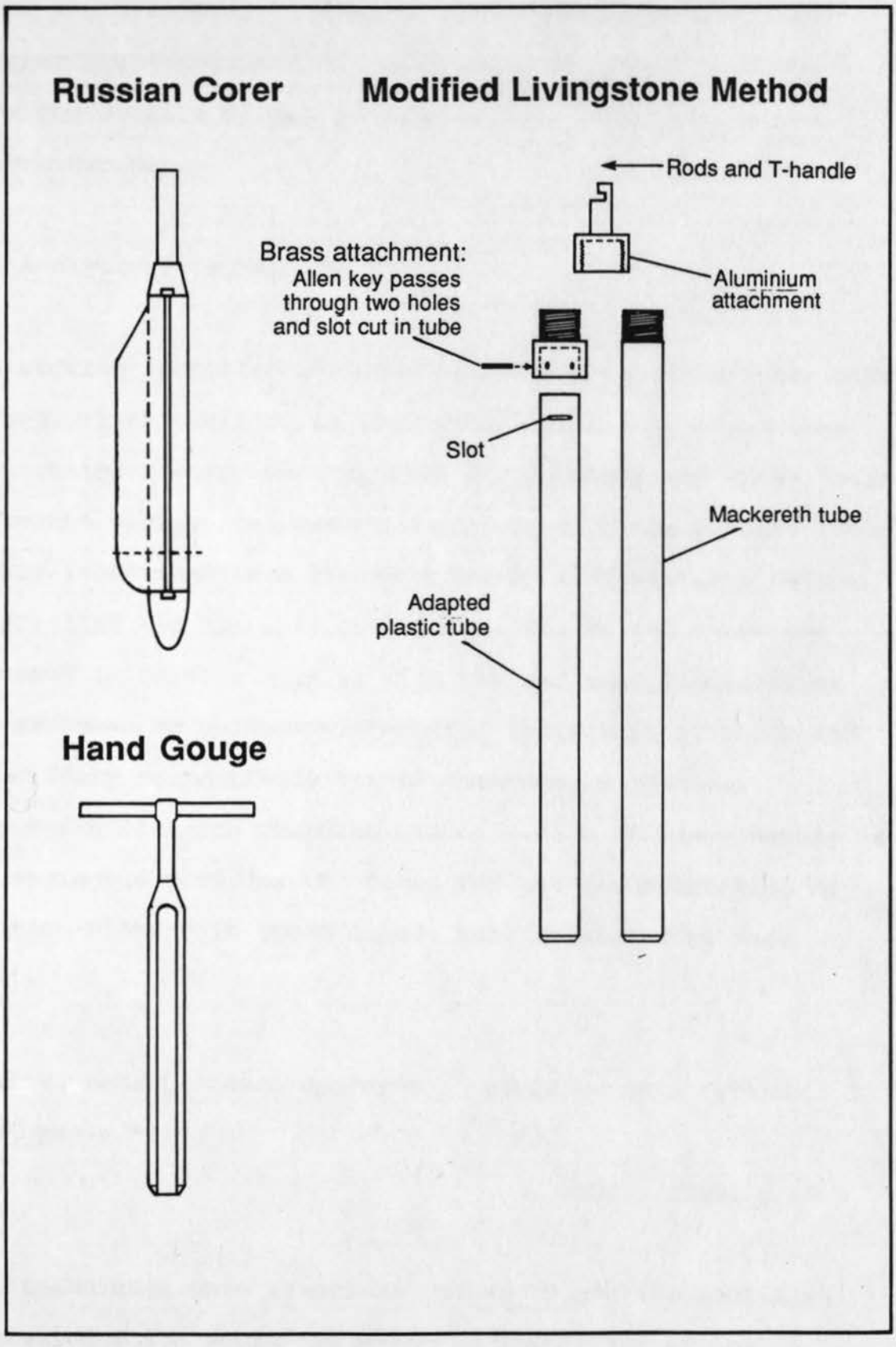
In the case of recent, soft lake sediment, it is generally not necessary to employ heavy percussion equipment with motor driven devices, but a simple hand-driven corer may be used such as the Russian sampler (Fig 2.12).

Of the end filling devices, the most commonly used are the Mackereth Corer (Mackereth, 1969) which relies on compressed air to drive the sampling tube into the sediment and the Livingstone Corer (Livingstone, 1955) which is a light-weight rod-operated piston sampler.

When coring was undertaken at Swanswell Pool in 1987, a 1 m Mackereth corer was initially used from a small rubber dinghy. This proved unsuccessful as the lake was shallow and the corer tended to bounce off the bottom without taking a sample. A modified Livingstone corer (Fig 2.12) was subsequently adopted in which a perspex tube of up to 2 m in length was driven into the sediment. This technique was successful in these shallow urban lakes and cores of up to 1.8 m long were retrieved. At Wyken Pool, the base of the lake was gritty which tended to split the end of the perspex tube. As a stronger alternative, a grey plastic tube with attachments illustrated in Fig 2.12 was used. A similar technique was also employed to retrieve river bed samples from the inflowing streams of Wyken Slough in order to minimise loss of fines when sampling.

Careful field and laboratory handling of the samples collected was important to minimise disturbance or

Fig 2.12 Coring samplers used in the study



contamination. Appendix 2 gives the details of the methods employed.

At the same time that cores were taken from the lake, bathymetry and sediment thickness were measured. Appendix 2 gives the details of the techniques used to construct the bathymetric map.

2.10 Analytical techniques

This section justifies the techniques used to address the aims and objectives outlined in Chapter 1. Table 2.21 summarises the techniques which were applied at Swanswell and Wyken Pools and to the various catchment components of Wyken Slough. The section is divided into two in order to differentiate between the physical and chemical properties. Fe, Mn and P are not discussed in section 2.10 ii with the sediment chemistry as they are used as palaeoenvironmental indicators of redox and productivity respectively rather than purely chemical characteristics. The changing concentration of heavy metals in lake sediments provides the focus for the reconstruction of pollution history in urban lakes, but, as stated by Smol (1992):

"Ideally, none of these approaches should be on a 'stand-alone' basis."

Smol (1992) p 49

Other techniques were therefore chosen to provide additional information which would allow better resolution of the

Table 2.21 Analysis carried out
a.) Swanswell and Wyken Pools
b.) Wyken Slough

a.	Swanswell Pool	Wyken Pool
Lake cores		
Stratigraphy	A	A
Water content	A	A
Organic matter	2	2
Particle size	1	2
Mineral magnetic measurements	A	A
Chemistry: total	4+12 surface	4+16 surface
sequential	1	1*
Mollusca	1	bulk
Phosphorus	4	4
Fe and Mn	4	4
^{210}Pb and ^{137}Cs activities	1	1

b. Wyken Slough	Marsh	Streams	Soil	Water quality
Stratigraphy	x	x	x	x
Water content	+	x	+	x
Organic matter	+	+	+	x
Particle size	x	x	x	x
Mineral magnetic measurements	+	+	+	x
Chemistry: total	+	+	+	x
sequential	x	x	x	x
dissolved	x	x	x	+
Mollusca	x	x	x	x
Phosphorus	+	+	+	+(PO_3)
Fe and Mn	+	+	+	x

Key
A = all cores or samples
2 = number of cores
bulk = bulk grab sample rather than a core
* = analysis undertaken by Ambridge, 1989
+ = samples analysed
x = samples not analysed

temporal record preserved in the lake sediments. Hence, physical properties such as those of water content, organic matter and stratigraphy have been used to provide a "fingerprint" of the core, and, allied with mineral magnetic measurements, enable correlation of the cores across the lake. Particle size down-core was measured to indicate changing sedimentating properties with time. Fe and Mn were used as proxy palaeo-redox indicators and P was measured to indicate whether eutrophication was becoming an increasing problem. Where possible, Mollusca preserved in the sediment column were also used to indicate past conditions in the lake. To put all these data into an absolute time frame, ^{210}Pb and ^{137}Cs dating were applied to selected cores at both sites.

Appendix 2 contains the details of how the analysis was carried out with information regarding instrumentation, chemicals and procedures and Table 2.21 summarises the techniques carried out on the sediments and soils retrieved from Swanswell and Wyken Pools, and Wyken Slough.

i. Physical parameters

It was considered important to record the physical parameters of lake sediments such as water content, organic matter and stratigraphy as any trends in the cores may reflect the biology and chemistry of the material deposited (Bengtsson & Ennell, 1986). Such parameters may also assist in core correlation where rates of deposition vary across the lake bed.

a. Stratigraphy

Variations in the material flux to lakes preserves a record of changes in the depositional and erosional regimes. When multiple coring exercises are carried out these changes can be monitored spatially and marker horizons can provide a means of correlation across the lake. This is useful when used in conjunction with other methods yielding correlatable horizons eg magnetic measurements (section 2.8e).

Stratigraphy was described using the Troels-Smith (1955) classification scheme. It is a comprehensive and widely accepted nomenclature (Goudie *et al.*, 1981) and as such iscomparable with other similar work. The classification is based on a combination of various physical properties from which the deposit can be defined without recourse to its origin or post-depositional history; unlike the genetic approach which has the disadvantage of requiring knowledge of the formation of the deposit before classification can be made (Goudie *et al.*, 1981; Berglund, 1986).

To be consistent with previous work, and to minimise bias in description, Munsell Colour Charts (1975) were used for colour comparison.

b. Water content.

Water content of lake sediments is distributed spatially in a characteristic way (Håkanson & Jansson, 1983) in that the lowest percentages of moisture are usually found in the shallowest areas, or near river mouths where coarser materials

dominate. The highest moisture content is usually found in the sediments located in the deeper parts of the lake. A downcore decrease in water content is usually observed due to compaction. The vertical, and hence temporal variation, in water content depends on:

1. The rate of sedimentation

2. The quality and characteristics of the deposit

3. The degree of compaction

4. The degree of bioturbation

5. The degree of disturbance within the catchment eg deforestation or building projects.

Water content and bulk density were measured using the procedures described in Appendix 2.

c. Organic matter

Organic matter was measured using loss on ignition at 450° C (Bengtsson & Ennell, 1986) and, under certain conditions, can be used as an estimate of organic carbon in the sample (Mackereth, 1966; Digerfeldt, 1972; Cato, 1977; Håkanson & Jansson, 1983). The correlation between loss on ignition and organic matter is reasonable for non-calcareous sediments

(Allen *et al.*, 1974; Håkanson & Jansson, 1983; Bengtsson & Ennell, 1986).

The estimation of carbonate content by loss on ignition at 850° C can only ever be a rough guide as various carbonate compounds volatalize at different temperatures (Ball, 1964). For the purposes of this study, however, estimates of organic matter and carbonate content by loss on ignition at the two temperatures discussed above were considered sufficiently accurate. The methodology is described in Appendix 2.

d. Particle size

The size of the particles can reflect three important characteristics of the composition of sediment (Håkanson & Jansson, 1983):

1. It reflects the processes of sedimentation

2. The capacity of the sediment for entrainment

3. The capacity of the sediment to bind pollutants, particularly when considering the partitioning of heavy metals by particle size (Förstner, 1977; Jones & Bowser, 1979; Förstner *et al.*, 1979; Förstner & Wittmann, 1981).

Research into the partitioning of heavy metals with varying particle size has established that there is usually an increase in heavy metal concentration with decreasing particle size. Förstner & Patchineelam (1980) and Förstner & Wittmann

(1981) present data from Lake Constance and the Lower Rhine in which particle sizes from 63 μm down to 0.06 μm are given, with the maximum concentration of Zn and Ni found in the 0.2 μm fraction.

Förstner & Patchineelam (1980) admit to the inaccuracy of fractionating heavy metals by means of particle size. This is due to the presence of coatings on the grains of Fe and Mn, carbonates and organic matter which all scavenge heavy metals from the environment. When analysing for particle size, sediments can either be left untreated by dispersing in distilled water or various treatments can be carried out on them to ensure separation of the individual grains. Treatment involves removal of cements, such as carbonate or Fe and Mn, binding the particles together. This usually involves an acid digestion which also removes any carbonates present (Foster *et al.*, 1985). The sediment is also treated with hydrogen peroxide to remove organic matter which occurs in long chains or flocculates and which would therefore give rise to spurious particle size results. As a result, the main sites for the binding of heavy metals in the sediments (section 2.3 ii c) are removed and the resulting particle size profile mainly reflects minerogenic elements alone; the fractions within the sediments which often contain the lowest concentration of heavy metals (Förstner & Wittmann, 1981). If the sediment were fractionated for heavy metals analysis on the basis of such a particle size profile, the resulting data would reflect the least important fraction in the sediment containing heavy metals. If, on the other hand, the sediment were analysed without pretreatment, the resulting profile would not reflect

ultimate particle size. In either case, heavy metal partitioning by particle size would seem to be meaningless in lakes with high organic matter, carbonate and iron and manganese concentrations. For the reasons outlined above, therefore, a particle size fractionation of heavy metals was not carried out at either site.

Particle sizing of the mineral fraction without a subsequent heavy metals analysis was carried out on two cores from Wyken Pool and one core at Swanswell Pool, lack of material due to other analyses prevented the analysis of a second core at Swanswell. Particle size was carried out in order to gauge the characteristics of sedimentation and the capacity of deposited sediments for resuspension (Håkanson & Jansson, 1983).

The cores used for particle size from Wyken Pool were taken from near the western inlet and near the eastern inlet (A3 and B1 respectively), that at Swanswell Pool (M8) was taken in a central location in order to avoid waste and brick rubble at the margins (Figs 2.12 a and b).

Details of procedure and sample preparation are described in Appendix 2. Particle size was measured using a Malvern 2600 Laser Diffractor. The M2600 is an optical measurement device which can sense the patterning of scattering monochromatic light. It is connected to a computer which converts the distribution of light energy on the detector rings into a particle size distribution.

The scattering of a beam of laser light by a particle is dependant on size, regardless of its motion or position in a beam of light. The diameter produced by the system is the

diameter of a sphere with the same volume as the particle, or volume diameter.

e. Mineral magnetic measurements

Mineral magnetic measurements were used in three main ways in this study:

1. To enable correlation of the cores across the lake once the grid of cores was complete (Bloemendal *et al.*, 1979; Oldfield *et al.*, 1979, 1983; Beckwith *et al.*, 1984; Hunt *et al.*, 1984; Stott, 1986; Thompson & Oldfield, 1986; Grew, 1990)

2. To aid in the tracing of sediment sources and characterisation of fluvial and limnic sediments. The magnetic characteristics of potential sources such as street dust, fly ash and deposits from the exhausts of internal combustion engines can be compared with the signal obtained from the sediments and a possible source inferred (Thompson *et al.*, 1975, 1980; Thompson & Morton, 1979; Oldfield *et al.*, 1983; Dearing, 1986, 1992; Flower *et al.*, 1989; Gaillard *et al.*, 1991).

3. To study any relationship between magnetic characteristics of the sediments and heavy metal concentrations. This was used to explore the possibility of magnetic characterisation serving as a surrogate measure for estimating certain pollutants present in lake sediments (Hunt *et al.*, 1984; Beckwith *et al.*, 1986; Brilhante, 1989; Foster *et al.*, 1991).

Magnetic measurements are versatile as they are quick to make, relatively cheap, repeatable and non-destructive (Oldfield *et al.*, 1983). They have been used in both lakes and rivers with varying climates in order to correlate cores, provide information on sediment sources and identify sediment mineralogy (Grew, 1990). They measure two characteristics of environmental materials; those occurring naturally and those induced artificially in the mineral assemblage by exposing the samples to varying magnetic fields.

Table 2.22 summarises the important types of magnetic behaviour associated with magnetic minerals and Table 2.23 summarises the characteristics of the various magnetic domains and their effect on associated behaviour. Based on these properties, the following measurements of lake sediments, soils, river bed sediments and marsh sediments were undertaken:

1. Low and high frequency susceptibility (χ_{lf} and χ_{hf})
   Units: $\mu m^3\ kg^{-1}$

2. Saturated Isothermal Remanent Magnetization (SIRM)
   Units: $mAm^2\ kg^{-1}$

3. Backfield Isothermal Remanent Magnetization (IRM)
   Units: $mAm^2\ kg^{-1}$

Fig 2.13 illustrates the hysteresis curve from which these measurements are derived. The following characteristics were calculated from the measurements outlined above:

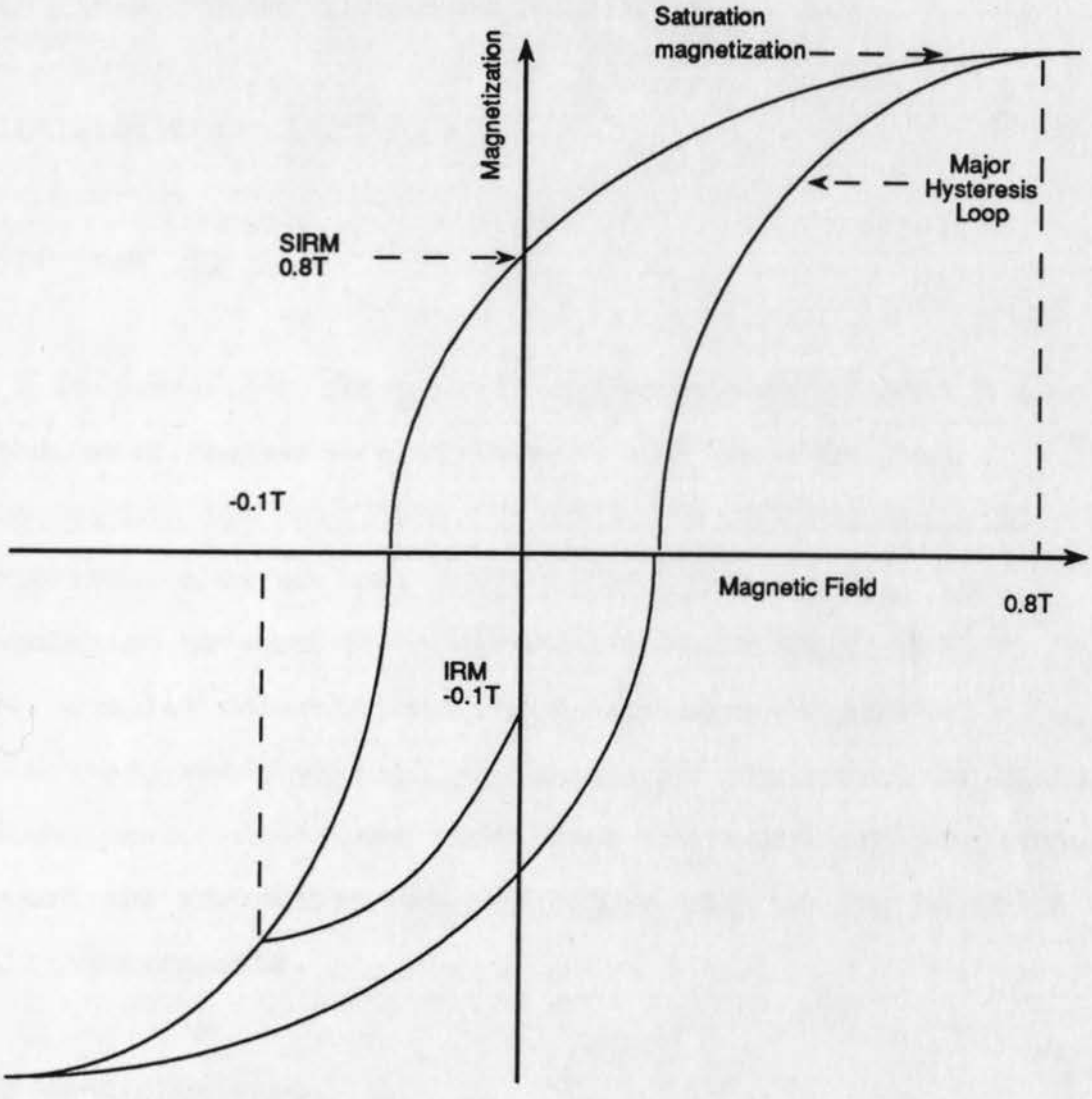
Table 2.22 Magnetic properties of minerals (adapted from Thompson and Oldfield, 1986 and Grew, 1990)

State	Result of application of magnetic field	examples
Diamagnetic (weakest)	Weak negative magnetisation not capable of holding remanence	Wood, water, quartz, calcite
Paramagnetic (2nd weakest)	Weak positive magnetisation not capable of holding remanence	Olivine, pyroxene Fe and Mn carbonates lepidocrocite
Antiferromagnetic (3rd strongest)	No net magnetisation capable of acquiring remanence	
As above but canted	Positive magnetisation in one direction	haematite goethite
Ferromagnetic Ferrimagnetic (1st and 2nd strongest)	Difficult to distinguish between the two. Strong magnetization, cabable of partial remanence acquisition	Fe and Mn ferrite magnetite and maghemite (rare)

Table 2.23 Magnetic domains and their effect on behaviour of magnetic minerals (adapted from Grew 1990)

Domain	size and magnetic characteristics	behaviour
Multidomain (MD)	Large crystals (>1.0 μm) Movement of domain walls characterises magnetisation	Partial magnetic field retained
Stable single domain (SSD)	No domain boundaries, each grain is its own domain	Higher remanences and more stable than MD
a. Superparamagnetic (SP)	<0.03 μm	Do not retain remanance at room temperature
b. Viscous (V)	SSD/SP boundary, grains found in soil	Delayed response to changes in the magnetic field High LFX
c. Pseudo single domain (PSD)	Between MD and SSD	Characteristics between MD and SSD.

Fig 2.13 Hysteresis loop and initial magnetisation curve (after Thompson and Oldfield, 1986)



1. Frequency dependent susceptibility either calculated on a mass specific basis (χ_{fd}) or as a percentage ($\chi_{fd\%}$)

   Units: $nm^3\ kg^{-1}$

2. S-ratio calculated from the ratio between IRM and SIRM.

3. High Field Remanent Magnetization (HIRM)

   calculated from: $\frac{SIRM\ (1-S)}{2}$

   Units: $mAm^2\ kg^{-1}$

Table 2.24 summarises the mineral magnetic measurements made. Lake sediments represent a mixture of all the processes occuring within the catchment. As such, the difficulty with characterization by mineral magnetic property is in distinguishing between the individual components of the mixture. Complex interactions occur dependant on mineral type, particle size, autochthonous processes and the effect of biota on the sediment. Additional techniques are therefore advisable to support and strengthen any inferences made on the basis of magnetic measurements.

ii. Sediment chemistry

When considering methods of chemical analysis it is necessary to consider the reasons for requiring these data. The necessity for chemical data in this study are twofold:

Table 2.24 Mineral magnetic measurements (from Dearing *et al.*, 1985; Thompson and Oldfield, 1986; Grew, 1990)

χ_{lf}	The ratio of magnetisation induced to the intensity of the magnetising field. It is an approximate measure of the total concentration of ferrimagnetic grains, and is sensitive to particle size. Values calculated on a mass specific basis.
χ_{fd}	The difference in susceptibility between low and high (χ_{lf}) frequency measurements. Can identify viscous grains and secondary magnetic minerals due to incorporation of soil particles. Values calculated on a mass specific basis (χ_{fd}) or percentage of total χ_{lf} ($\chi_{fd\%}$).
SIRM	The remanence retained by a sample upon removal from a saturating magnetic field. SIRM indicates volume concentration of magnetic minerals and also changes in grain size.
IRM	Reflects the approximate concentration of remananence carrying haematite.
S-ratio HIRM	Demagnetising parameters, these are useful in the identification of grain size components in homogeneous samples and the proportion of ferrimagnetic to antiferromagnetic minerals.
SIRM / χ_{lf}	Scattergrams used to indicate variations in grain size in single mineral samples. In a mixture, the ratio can indicate differences in the proportions of minerals in the mixture.

1. To assess the total amount of heavy metals in the sediments, and calculate the flux and accumulation rate. This can be applied to an assessment of background levels and subsequent changes in concentration and loading.

2. To partition the heavy metals according to sites within the sediment and hence assess their availability should environmental conditions change.

Two methods are therefore required in order to fulfil these aims; a method giving the concentration of heavy metals in the bulk sediment, or a total digest, and a method which yields the concentration of heavy elements in selected fractions within the sediments, or a sequential digest. There are other methodologies for obtaining data on heavy metal concentration in sediments which are outlined in Table 2.25. This Table shows that the atomic absorption method is sensitive, accurate (Förstner & Wittmann, 1981) and is the most widespread method used in the analysis of water and effluents (Bengtsson & Enell, 1986).

a. Total digestion method

The wet digestion method was chosen for this study to conform with similar studies carried out in the English Midlands (Foster *et al.*, 1987, 1991; Foster & Dearing, 1987a). The facilities were readily available and the techniques well known.

Table 2.25 Comparison of various methods of trace metal analysis (after Förstner and Wittmann, 1981)

Analytical technique	Approximate range of concentration (g)							
	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	10^{-15}	10^{-16}
Gravimetry	...							
Titrimetry	.....							
Colourimetry	_.....	.....						
Fluorescence	_____	.....						
Kinetics	_____	_____	_____	.....	.....			
Inverse voltametry	_____	_____	.....	.....				
Flame emission spectroscopy	_____	.....						
Atomic absorption spectrophotometry (AAS)	_____	.....	.....					
Non-flame AAS	_____	_____	_____	.....	.....			
Gas chromatography	_____	_____	.....	.....	.....			
X-ray fluorescence (XRF)	...							
Radiometry	_____	_____	_____	_____	_____	_____	.....	.....
Activation analysis	_____	_____	_____	_____	.....	.....		
Mass spectrometry	_____	_____	_____	.....	.....	.....	.....	

_____ applicable in most circumstances
..... applicable in single cases

Table 2.26 Total digestion methodologies (from Förstner and Wittmann, 1981).

1. Hydrofluoric acid (HF) digestion

Usually used in combination with H_2SO_4, $HCLO_3$ and HNO_3. HF dissolves the basic silica and silicate matrix of the sediment. Metal sulphates are often difficult to dissolve, combination with $HClO_3$ produces perchlorates which are easier to get into solution (Förstner and Wittmann, 1981). Addition of HNO_3 reduces the possibility of explosion.

2. HCl - HNO_3

Useful for volatile elements such as Hg, As and Cd. Provides a high degree of metal extraction, but silicates are not completely dissolved. Metals in association with organic matter are dissolved and some of the metals in the crystal lattices are removed (Agemian and Chau, 1976).

3. Lithium metaborate fusion

Results from fusion techniques are not comparable with wet digests (Greenwood, 1991), but it is faster than acid digestion and dissolves most minor minerals (Alloway, 1989).

All of the above provide a solution of heavy metals which readily pass through an AAS.

In order to measure the concentrations of elements in sediment by the wet digestion method, they must first be dissolved. Dissolution is achieved by digestion in strong acid solutions. There are various digestion methodologies, ranging from vigorous treatment with hydrofluoric acid and aqua regia to less comprehensive digests of concentrated acids (Table 2.26). The laboratory facilities available were not considered suitable for the use of hydrofluoric acid and a less vigorous method was used which nonetheless gives a high degree of metal extraction , but did not dissolve residual silica. Alloway (1989) called this "pseudo-total analysis" but noted that, as most heavy metal pollutants are not bound to the silicate phases, a digest solution of concentrated acids other than HF would prove vigorous enough to dissolve heavy metals not bound to the silicates. This method has also been used in previous related studies and, by using the same methodology, the data should be directly comparable (Renberg, 1986; Foster *et al.*, 1991).

b. Sequential extraction

Techniques to determine the associations of elements with specific sedimentary phases are useful to assess the potential availability of toxic compounds for biological uptake (Salomons & Förstner, 1980). It is important to know this for four main reasons:

1. To assess whether the sediments are a permanent sink for trace metals or whether remobilization is likely to occur.

2. To assess the bioavailability of the contaminants in the sediments for aquatic life.

3. To assess the behaviour of the pollutants in dredged material during and after disposal to landfill or upon land spreading.

4. To assess the subsequent bioavailability of the trace metals in the landfill site.

The total concentration of heavy metals within the bulk sediment gives no information on which of the elements may take part in short term geochemical processes or are bioavailable. Tessier *et al.* (1979) go further :

"Use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable."

Tessier *et al.* (1979) p 844

In order to partition the metals within the sediment a sequential extraction procedure was needed. There are a wide range of sequential digestion procedures in use (Table 2.27 a), but unfortunately none of these are comparable. A digest had already been carried out on one core at Wyken Pool (Ambridge, 1989) and it was decided to use the same methodology on one core at Swanswell Pool, that given by Tessier *et al.* (1979) (Table 2.27 b). Only one core at each

site was sequentially digested mainly due to the length of time taken to perform the analysis. Up to 6 weeks was needed to process 16 samples and the resultant solutions often proved difficult to analyse on the atomic absorption spectrophotometer (AAS) as deposit built up on the burner sometimes necessitating the instrument having to be switched off, allowed to cool and cleaned after every 4-5 samples (see details in Appendix 2).

2.11 Palaeoenvironmental indicators

Lake trophic level and hydroseral development can be assessed by means of the remains of biota preserved in the sediment at the bottom of a lake. P, Fe and Mn reflect changing trophic level and redox conditions, so a combination of these factors is useful in determining changing environmental conditions with time.

i. Mollusca, pollen and diatoms

The use of pollen, diatoms, molluscs, etc. to infer environmental change, particularly during the Quaternary, is well documented (Sparks, 1961; Birks & Birks, 1980; Lowe & Walker, 1984; Faegri & Iverson, 1989). The change in species diversity and numbers within a sediment core may correlate with fluctuations in heavy metal concentration indicating the response to increases in urbanisation in the catchment by invertebrates and flora.

Table 2.27 a Sequential digest methodologies after Förstner and Salomons (1981 b)

Sediment fraction	Extraction methodology
Extractable	BaCl, MgCl, NH_4OAc
Detrital/ non-detrital	EDTA, 0.1M HCL, 0.3M HCl, 0.5M HCl, 0.1M HNO_3
Mn and Fe	Acidified hydroxylamine, ammonium oxalate, hydroxylamine-acetic acid, dithionite/ citrate
Carbonate	CO_2 treatment, acidic cation exchange, NaOAc/ HOAc (pH 5)
Organic	H_2O_2, H_2O_2-NH_4OAc, H_2O_2-HNO_3, organic solvents, 0.5N NaOH, 0.1N HaOH/ H_2SO_4, Na hypochlorite-dithionite/ citrate
Detrital silicates	HF/ $HCLO_4$

Table 2.27 b Fractions selected for sequential chemical analysis (After Tessier *et al.*, 1979)

Fraction	Form of heavy metal	Sensitivity to environmental change
1. Exchangeable	Adsorption to clays, hydrated iron and manganese oxides and humic acids	Changes in water ionic composition
2. Bound to carbonates	association with sediment carbonates	Changes in pH
3. Bound to Fe and Mn oxides	Nodules, concretions and cements of Fe and Mn oxides scavenge trace metals	Thermodynamically unstable under anoxic conditions ie. low Eh
4. Bound to organic matter	Living organisms, detritus, coatings on mineral particles	Degradation of organic matter under oxidising conditions can release soluble trace metals.
5. Residual	Primary and secondary minerals holding metals in crystal lattices	Not usually released under normal range of environmental conditions.

Pollen grains at both sites were found to be too poorly preserved and too few in number to be useful. A preliminary examination of 5 samples from one core from Swanswell Pool (R Flower, University College, London) found that diatoms were well preserved and numerous. However, lack of time to extract and identify diatom remains meant that these procedures were not attempted.

Mollusca were well represented and preserved at Swanswell Pool, but less so at Wyken Pool. One core from Swanswell Pool was therefore analysed for Mollusca to infer the changing environmental conditions at the site with time. Grab samples of sediment at the mud-water interface from Wyken Pool were taken to assess the present-day conditions at the site for freshwater Mollusca.

ii. Phosphorus

The phosphorus content of the sediments was measured in order to assess the trophic status of the lakes and changing trophic level through time, rather than as a simple measure of chemistry. The possibility of eutrophication in shallow polluted lakes is a common problem (Cooke *et al.*, 1986; Ryding & Rast, 1989). Ryding & Rast (1989) point out that even if the source of the excess nutrients is decreased a net outflow of phosphorus continues for some time afterwards. This has future management implications should the sediments have a high phosphorus content.

Total phosphorus was measured using the method described in Foster *et al.* (1986b) so that the analysis was comparable

with data from other sites. P analysis was undertaken by colourimetry (details in Appendix 2) on the digests obtained from the total extraction procedure, details of which are also given in Appendix 2.

iii. Fe and Mn.

Fe and Mn concentrations reflect changing redox conditions at the mud-water interface (Oldfield, 1977). Changing redox conditions reflect phosphorus exchange at the sediment-water interface and thus trophic level (Håkanson & Jansson, 1983). A combination of palaeoenvironmental indicators, phophorus, Fe and Mn concentrations hence provide an indication of nutrient availability and utilisation within the lake and also the activity of the heavy metals scavenging factors as shown in Fig 2.6. Fe and Mn determination was carried out by AAS on the digests obtained from the total extraction, details of which are given in Appendix 2.

2.12. Dating.

The radioisotopes ^{210}Pb and ^{137}Cs were used to date the sediments as the period of interest is less than 150 years. Facilities were available within the Physics Department at Coventry University to carry out the analysis.

i. ^{210}Pb

The ^{210}Pb dating method was devised by Goldberg in 1963

and has been in common use over the last 30 years (Olsson, 1986). ^{210}Pb has a half life of 22 $\pm$ 0.22 years and should therefore be useful for dating sediments up to 150 years of age.

Figure 2.14 illustrates the two sources of ^{210}Pb to the lake sediments :

1. Supported, or that derived from erosion within the catchment

2. Unsupported, or that transported in the atmosphere and deposited on the lake surface.

In order to date sediments using this method, it is necessary to be able to distinguish between the total ^{210}Pb and the supported ^{210}Pb.

There are three assumptions implicit when dating sediments using this method:

1. That the ^{210}Pb does not migrate in the sediment column

2. That the flux of ^{210}Pb to the sediments is constant

3. That the residence time of ^{210}Pb in the sediments is constant.

The age of the sediment at any particular depth is calculated from its unsupported ^{210}Pb activity relative to

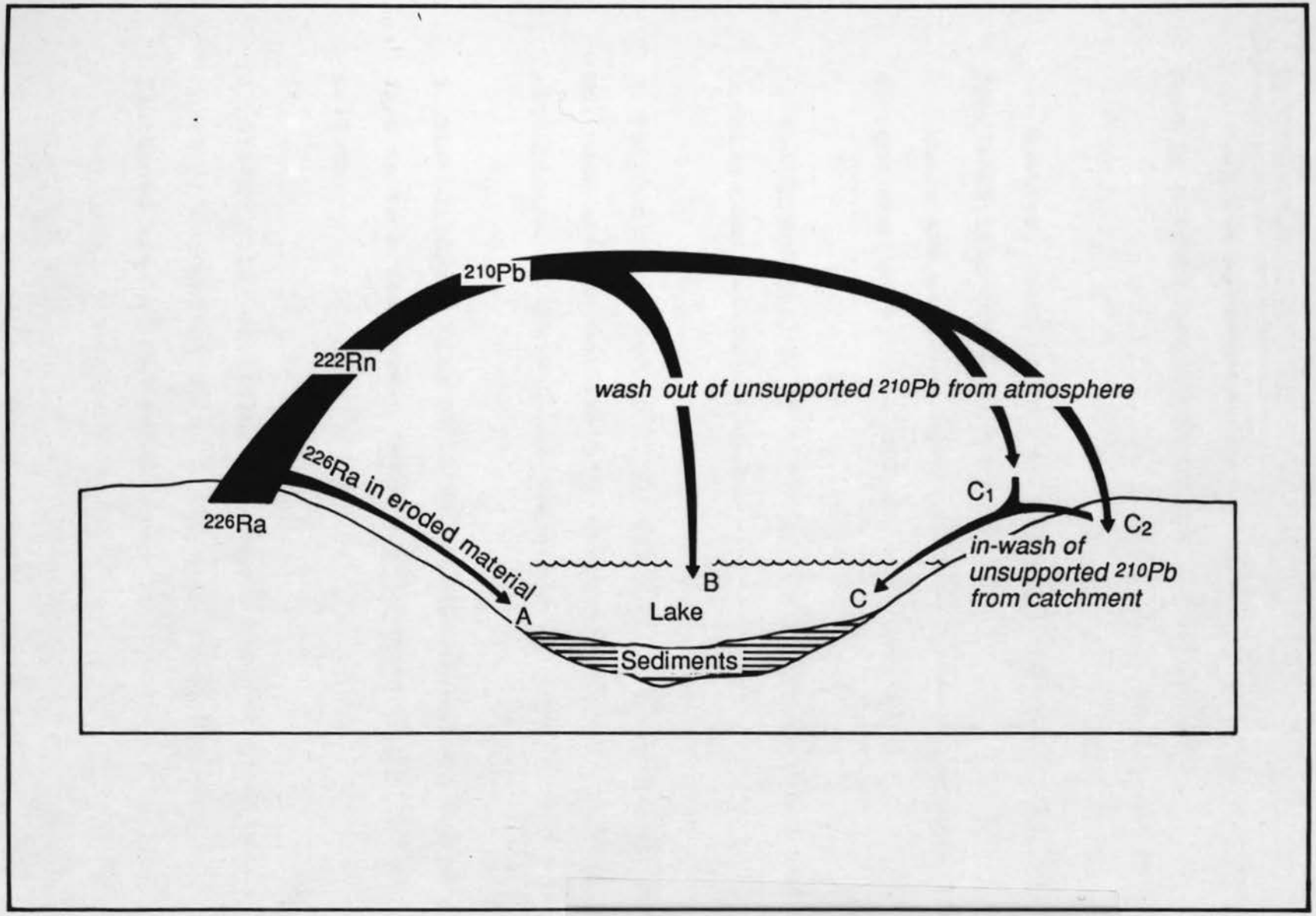


Fig 2.14 Sources of ^{210}Pb to sediments (Goudie *et al.*, 1981)

that at the surface and the radioactive half life (Pennington *et al.*, 1976).

Olsson, (1986) recommends that

"..a few determinations from every core ...from the top down to a level corresponding to 100-150 years"

Olsson (1986) p 299

However, lack of project funding meant that only one core from each lake could be dated.

There are several variables which have to be taken into account when using this method:

1. The concentration of ^{210}Pb can be elevated near a coal burning power station (Eakins, 1983)

2. The concentration of ^{210}Pb can also be elevated if there has been any nuclear testing, although this is unlikely to be significant in the English Midlands.

3. The residence time of ^{210}Pb in the atmosphere ranges from 9 days up to a few weeks, therefore deposition may not be uniform.

4. Bioturbation or mixing may smooth out the profile and the curve of concentration of ^{210}Pb with depth may show a flattened area at the crest.

5. Some mobilization of lead in interstitial water may occur, especially if the sediment has a high water content.

6. Sediment resuspension or focusing may give a low ^{210}Pb level where appreciable erosion has taken place, and enhanced lead levels where focussing has occurred (Oldfield & Appleby, 1984).

7. Catchment derived unsupported ^{210}Pb may prove to be a significant source of error. This may be due to disturbance of the catchment when, for example, residential housing estates or industrial complexes are built and is obviously a factor to consider in urban areas (Oldfield & Appleby, 1984).

8. Variable allochthonous sedimentation may affect the ^{210}Pb record, but Oldfield & Appleby (1984) report that it is not significant as a source of error.

Sediments are dated using this method by determining both the total ^{210}Pb and the supported ^{210}Pb. The latter is found by measuring the ^{226}Ra, and subtraction of this value from the total ^{210}Pb, represents the unsupported ^{210}Pb in the sample.

ii. ^{137}Cs

The above limitations illustrate the need for more than one dating method to be carried out to verify results. Another well-documented method for radiometrically dating sediments is that of measuring ^{137}Cs. This isotope has been artificially

produced as a consequence of nuclear weapons testing from 1954 and accidents such as that of Chernobyl in 1986.

Pennington *et al.* (1976) used ^{137}Cs and ^{210}Pb to date the recent sediments of Blelham Tarn in the English Lake District and found the radioisotopic dates to be consistent. Pennington's study was also able to use palaeomagnetic measurements as well as ^{14}C to confirm the consistency of the dating methods, and a total of 8 cores were analysed.

The fallout of ^{137}Cs began in 1954 and the peak in activity took place in 1963. As with ^{210}Pb, there are several factors that have to be considered when using ^{137}Cs as a dating tool :

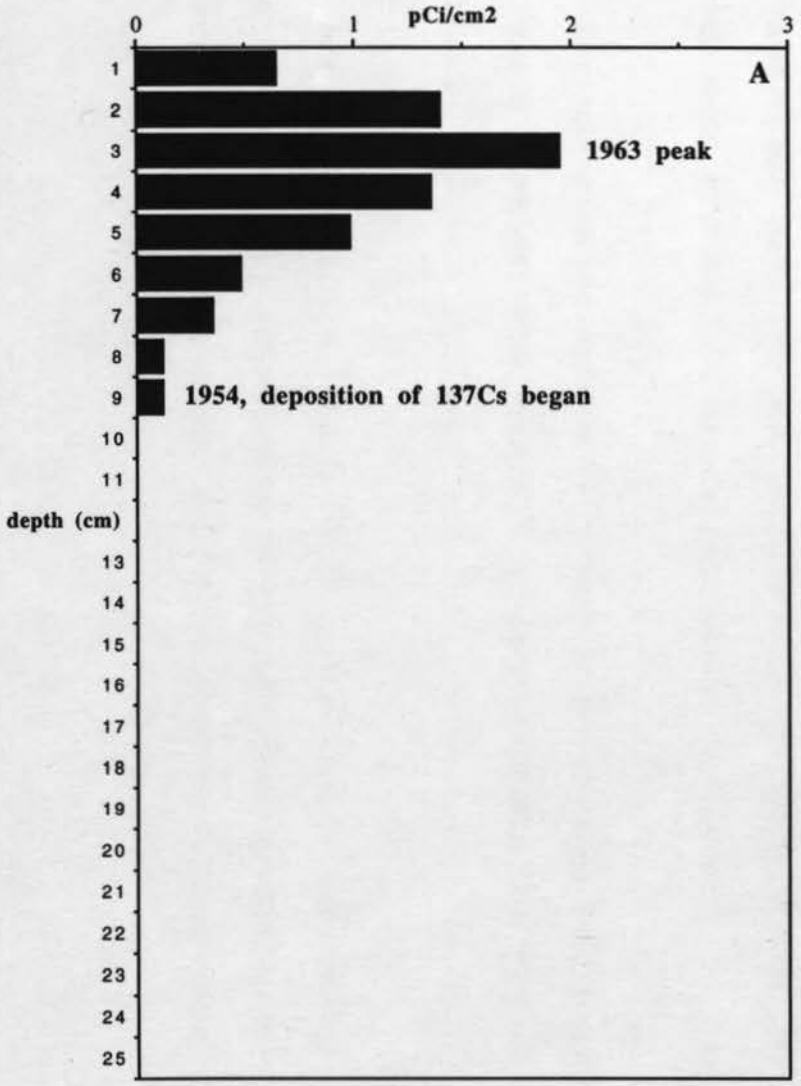
1. Bioturbation is a problem in that it can smooth out the record.

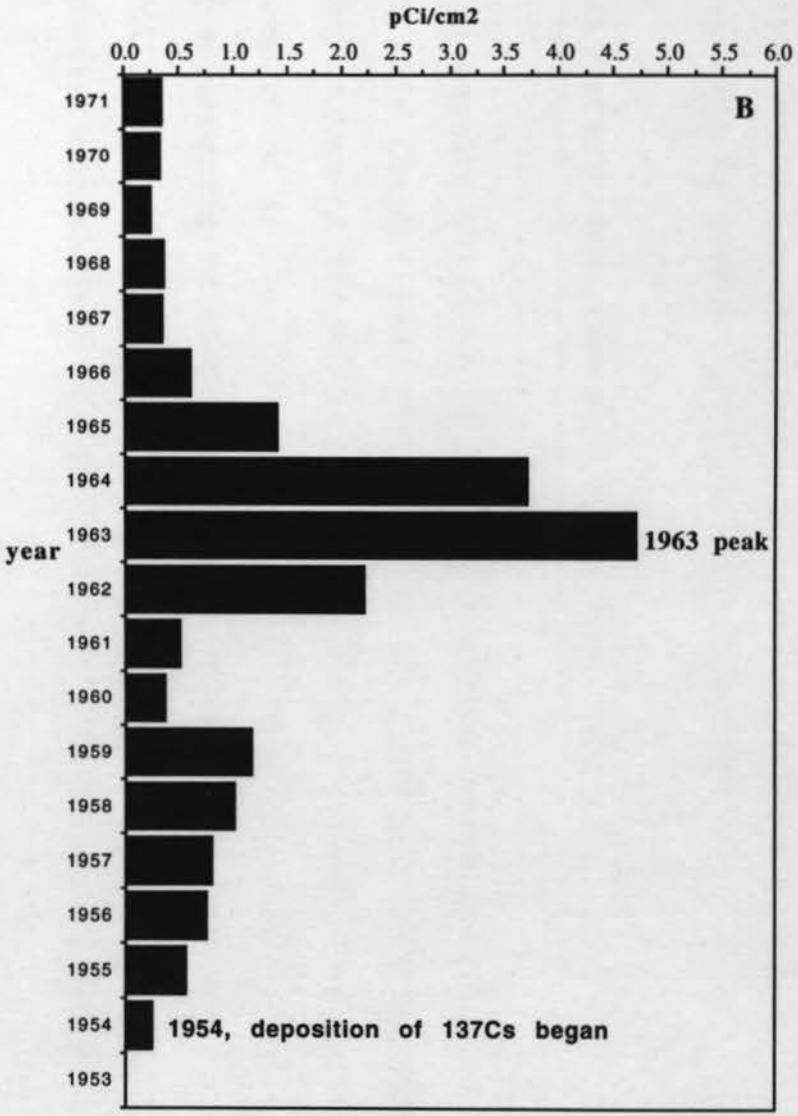
2. ^{137}Cs may be mobile in the sediment under certain conditions

3. Delayed ^{137}Cs input from soil erosion can be a source of error.

Dating using this method involves ascertaining the depth at which ^{137}Cs is measurable in the lake sediment; this would represent 1954 when fallout began. The rise in ^{137}Cs content can then be confirmed by a peak in activity representing 1963. Fig 2.15 shows the estimated annual deposition of ^{137}Cs at Windermere (Pennington *et al.*, 1973b) and the actual distribution of ^{137}Cs in the upper 25 cm of the sediments at

Fig 2.15 Deposition of 137Cs to the sediments of Lake Windermere
a. Actual deposition b. Annual deposition (after Pennington et al 1973)





Windermere. The 1963 peak in activity is marked on the traces and 1954 is marked for when fallout began.

2.13 Statistical analysis

The results obtained from the analytical techniques described in this Chapter were subjected to statistical analysis. The objectives of these tests were to identify whether particular properties of the sediments could be discriminated independantly or whether they shared a high degree of colinearity. In order to identify these characteristics, statistical analyses aimed to answer the following questions:

1. Are the data bases suitable for parametric statistical tests?

2. Are there correlations between magnetic parameters, in which case are some of the measurements redundant?

3. Are there correlations between the individual heavy metals, in which case can the presence of one indicate the presence of others?

4. Are there correlations between the magnetic parameters and the heavy metals, in which case can magnetic measurements serve as a surrogate measure of heavy metals either as a group or as individual elements?

5. Can a small number of common properties be extracted from the large number of variables?

6. How consistent are the results from the 4 cores taken from each of the lakes?

7. What is the relationship between the catchment components at Wyken Slough and the sediment deposited in the lake?

Statistical analysis was carried out using SPSS PC.

2.14 Summary

This chapter has set out the rationale behind the present study in terms of previous limnological work. It has identified a gap in studies of pollution history in that few studies of entirely urban lakes have been carried out. Using a paired lake catchment approach, it suggests a practical framework using a variety of techniques to address this deficiency. These techniques include a sampling strategy, chemical and physical analysis and the subsequent statistical testing of the results obtained.

Chapters 4, 5 and 6 describe the results obtained from Swanswell Pool, Wyken Pool and the Wyken Slough catchment respectively, in terms of the framework outlined in this Chapter.

Chapter 3

Site description and histories

3.1 Introduction

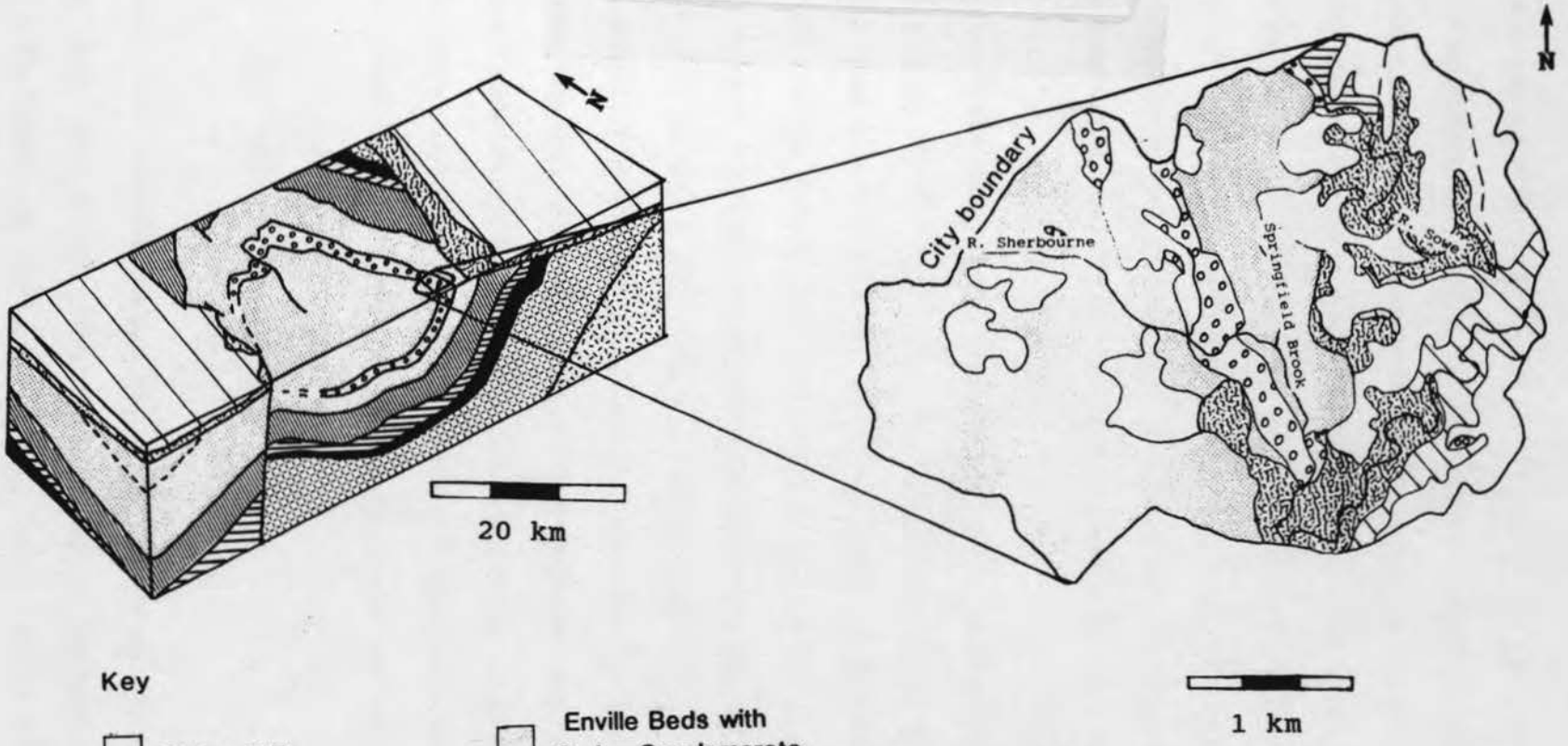
This chapter describes the development of the sites as indicated by documentary evidence, and their current appearance. Section 3.1 discusses the background to the Coventry region in terms of its underlying geology, geomorphology and climatology. Section 3.2.3 traces the origins of the Industrial Revolution in the City of Coventry. This has an important bearing on changing contaminant loadings through time, as discussed in Chapter 7. The catchments of Swanswell Pool and Wyken Slough are considered in Section 3.3 and their histories discussed in Section 3.4.

3.2 Background to the Coventry region

3.2.1 Geological and Geomorphological setting

Coventry is situated in Midland England on the eastern side of the East Warwickshire Plateau (Fig 3.1), an inlier in the New Red Sandstone of the Midland Plain, which is cut by several fast flowing streams, generally flowing in a westerly or southerly direction (Coventry Geographical Association, 1971).

Fig 3.1 Geology of the Coventry area (after Dix and Hughes, 1960)



Although strategically the site of the City was not important, Coventry initially developed on the slightly higher ground to the south of the River Sherbourne with the land sloping away on all sides, particularly to the east, where there is a resistant band of Carboniferous sandstone and conglomerate. The surface strata in the Coventry area are the Upper Coal Measures of the Keele and Enville beds. The geological sequence generally becomes younger in a southerly direction.

The Keele beds are clays and sandstones and yield reasonable soils when weathered. The Enville Beds are red clays, marls and sandstones with occasional conglomerates and breccias. The sandstones form an extensive aquifer which has several wells and boreholes providing potable water as well as water which can be used for industrial purposes.

To the west of Coventry, lying unconformably on the Carboniferous rocks, are the Keuper Sandstones and Marls of Triassic age. Any remaining deposits are of alluvium or are Pleistocene deposits such as the sand and gravels which are well represented to the east of the City (Old *et al.*, 1990).

3.2.2 Hydrology and climate

The River Sherbourne flows southeast across the present day City to join the River Sowe and in doing so breaches the "cliff" of conglomerate and sandstone. This produces a flat-floored, fairly steep-sided valley with a narrow floodplain.

The Pickford Brook joins the Sherbourne from the east and the Radford and Swanswell Brookes join the River Sherbourne from the north with a prominent spur of sandstone separating the latter two at about 130 m OD.

Fig 3.2 shows the relief and drainage of the Coventry area. The highest points are to the west at an altitude of about 150 m OD. To the north of Swanswell Brook the less resistant Upper Coal Measures present an area of flat land at 100-120 m OD. An extension of this flatter area to the south of the river forms the watershed between the Sherbourne and the streams to the southwest which join the Finham Brook.

Figures 3.3 a and b summarise the data for the Coventry meteorological record (Cockerton, 1991). The bar charts represent two years, 1990 and 1977 and indicate the average total sun and rain (Fig 3.3a) and minimum, maximum and average temperature (Fig 3.3b) for each month with the average over the year for temperature data at 'month' 13. The climate represented is a typical northern hemisphere temperate one with highest temperatures and sunshine hours recorded in May to August and the wettest months in November to February. The mean annual rainfall for the region is 678 mm from data taken over 125 years from 1867 to 1992 (Sheard, 1994).

3.2.3 The historical development of Coventry

From nearly 70 inhabitants reported in the Domesday Survey of 1086, Coventry grew to become an important centre

Fig 3.2 Topography of the Coventry area (after Foster *et al.*, 1994)

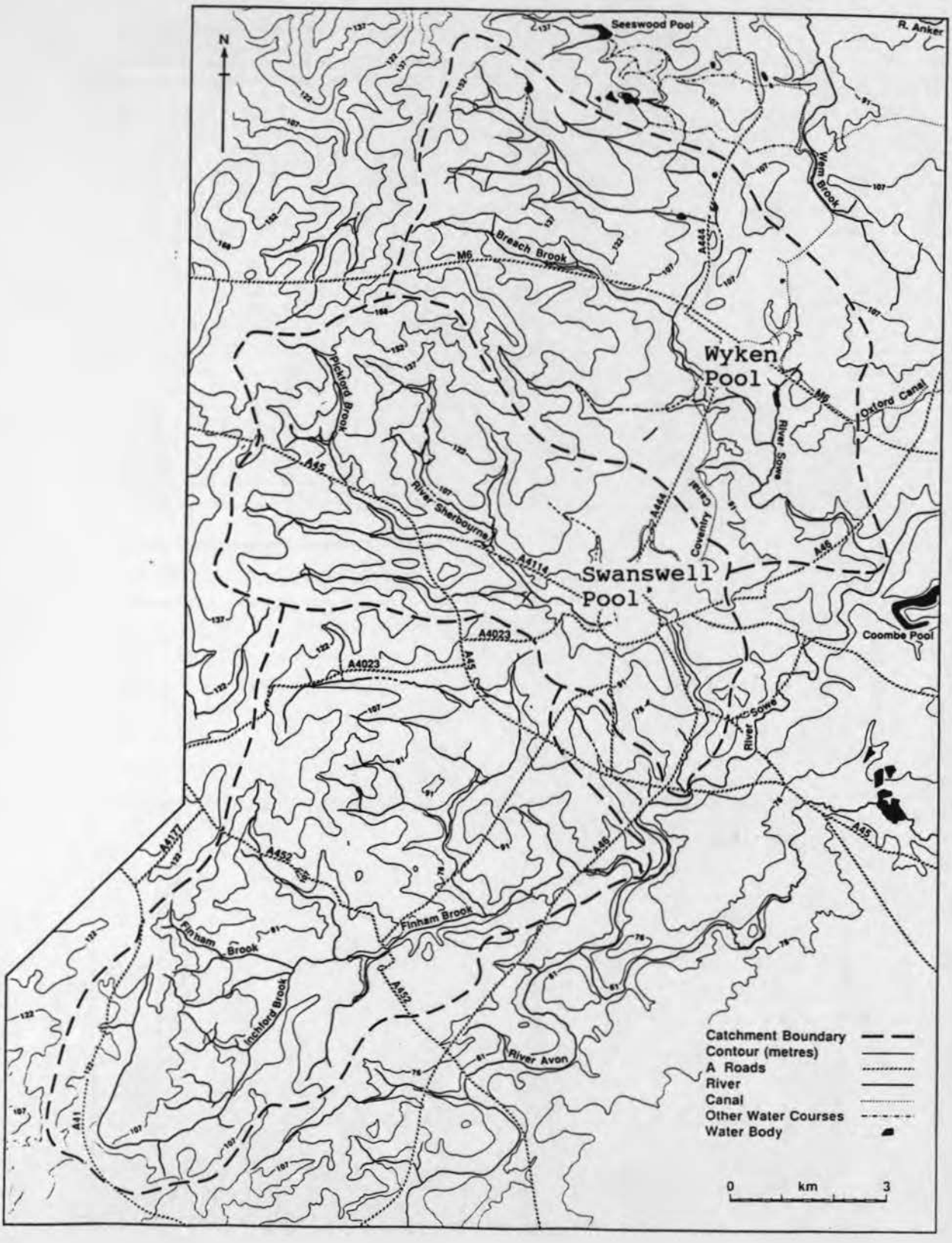
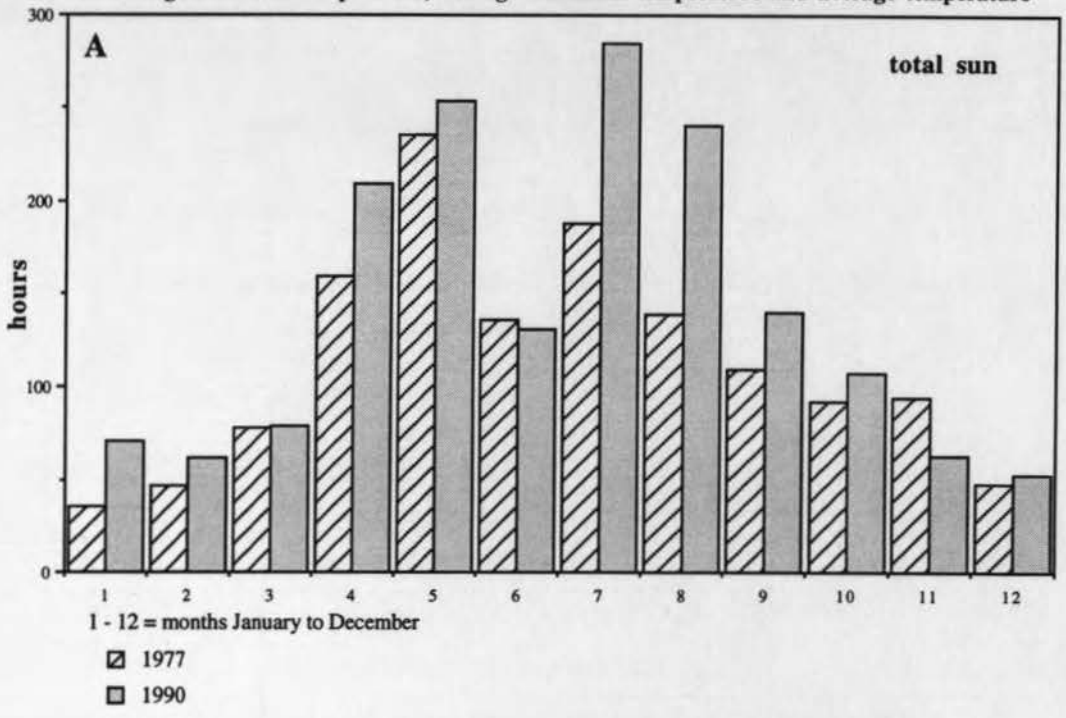
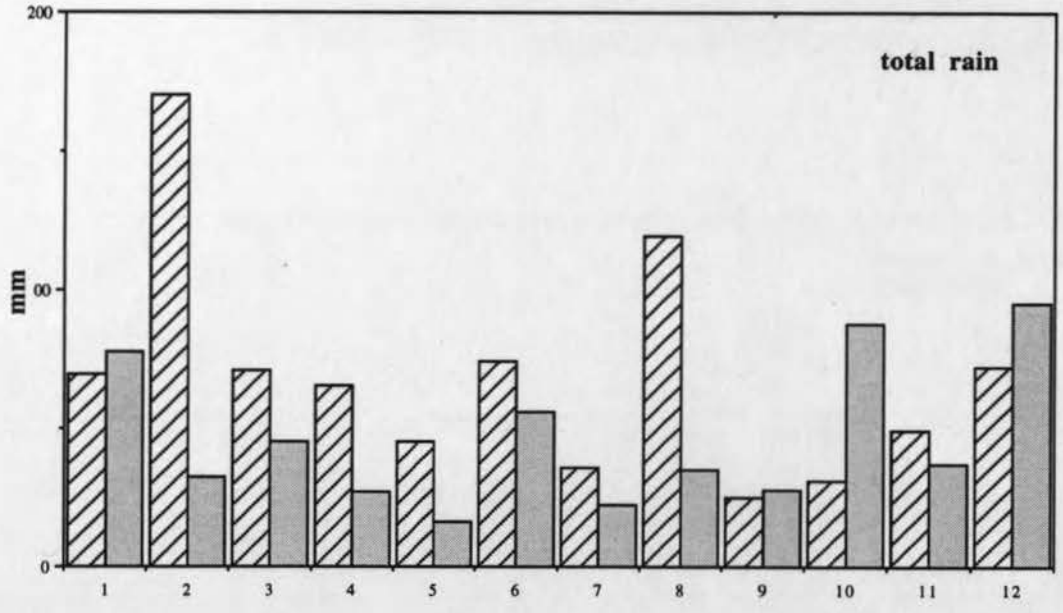
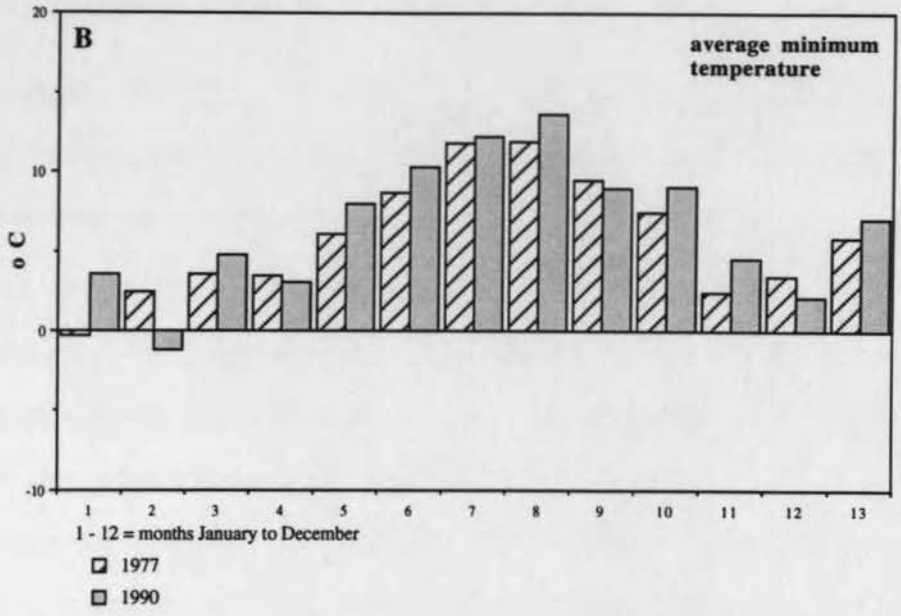
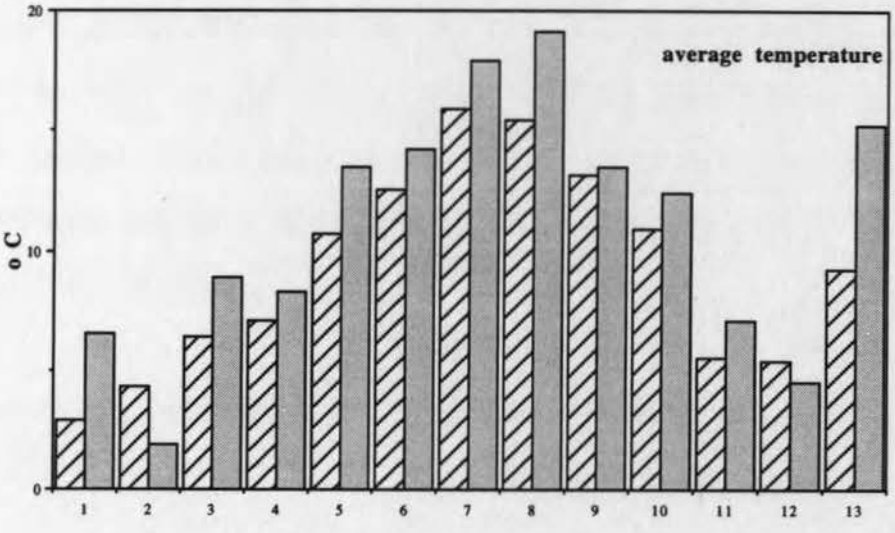


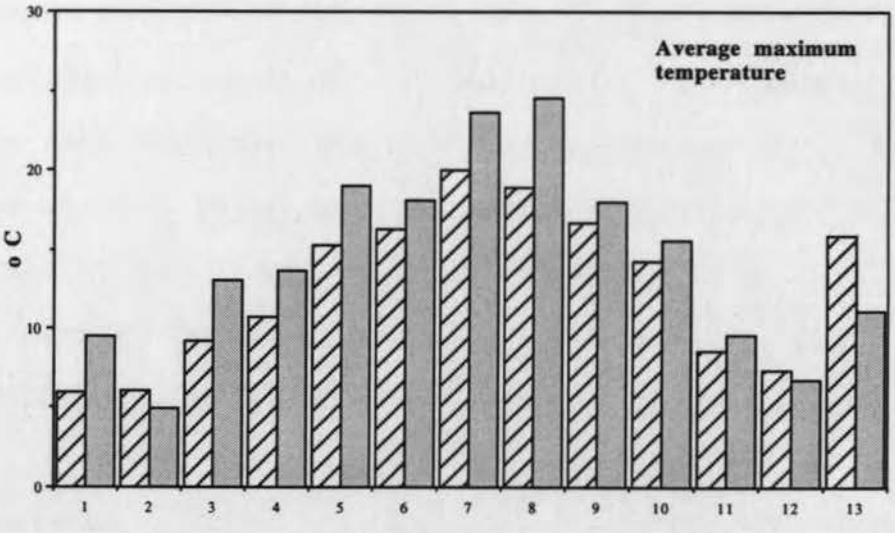
Fig 3.3 Coventry area climatological data
a. total sun and total rain
b. average minimum temperature, average maximum temperature and average temperature






B
average minimum temperature
o C
20
10
0
-10
1 2 3 4 5 6 7 8 9 10 11 12 13
1 - 12 = months January to December
1977
1990


average temperature
o C
20
10
0
1 2 3 4 5 6 7 8 9 10 11 12 13


Average maximum temperature
o C
30
20
10
0
1 2 3 4 5 6 7 8 9 10 11 12 13

for the manufacture of silk ribbons and watches between 1765 and 1850. When competition suffocated these industries, the late nineteenth and early twentieth centuries saw the rise of the bicycle and motor industries as well as aeroplane manufacture, munitions factories and machine tools. The population expanded, particularly in the twentieth century (Fig 3.4), and the City expanded with it (Fig 3.5).

By 1930, however, aided by the general slump of the 1920's, 40 firms ceased production. The slimmed down motor manufacturers were able to use their modern methods to effect during the Second World War and the technology was expanded into aeroplane manufacture with the building of new premises.

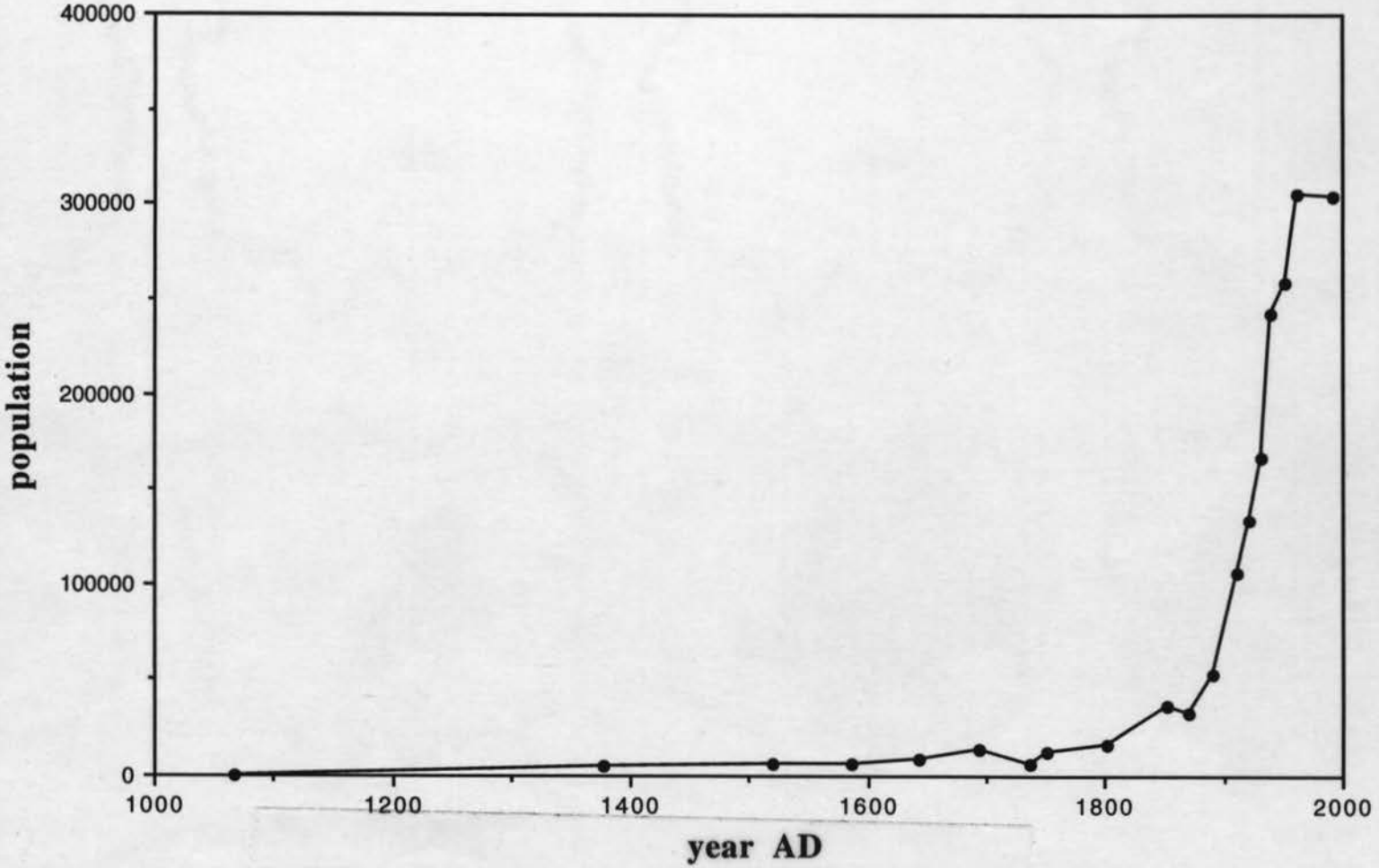
Whilst the larger factories engaged in heavy manufacture closed, for example Smith's Stamping Works, Albion Drop Forgings and Hawker Siddeley,

"...the premises left vacant..were easily let as trading estates." Richardson (1972) p 141

and industrial estates, such as at Bayton Road in the catchment of Wyken Pool, were built in the 1960's and 70's.

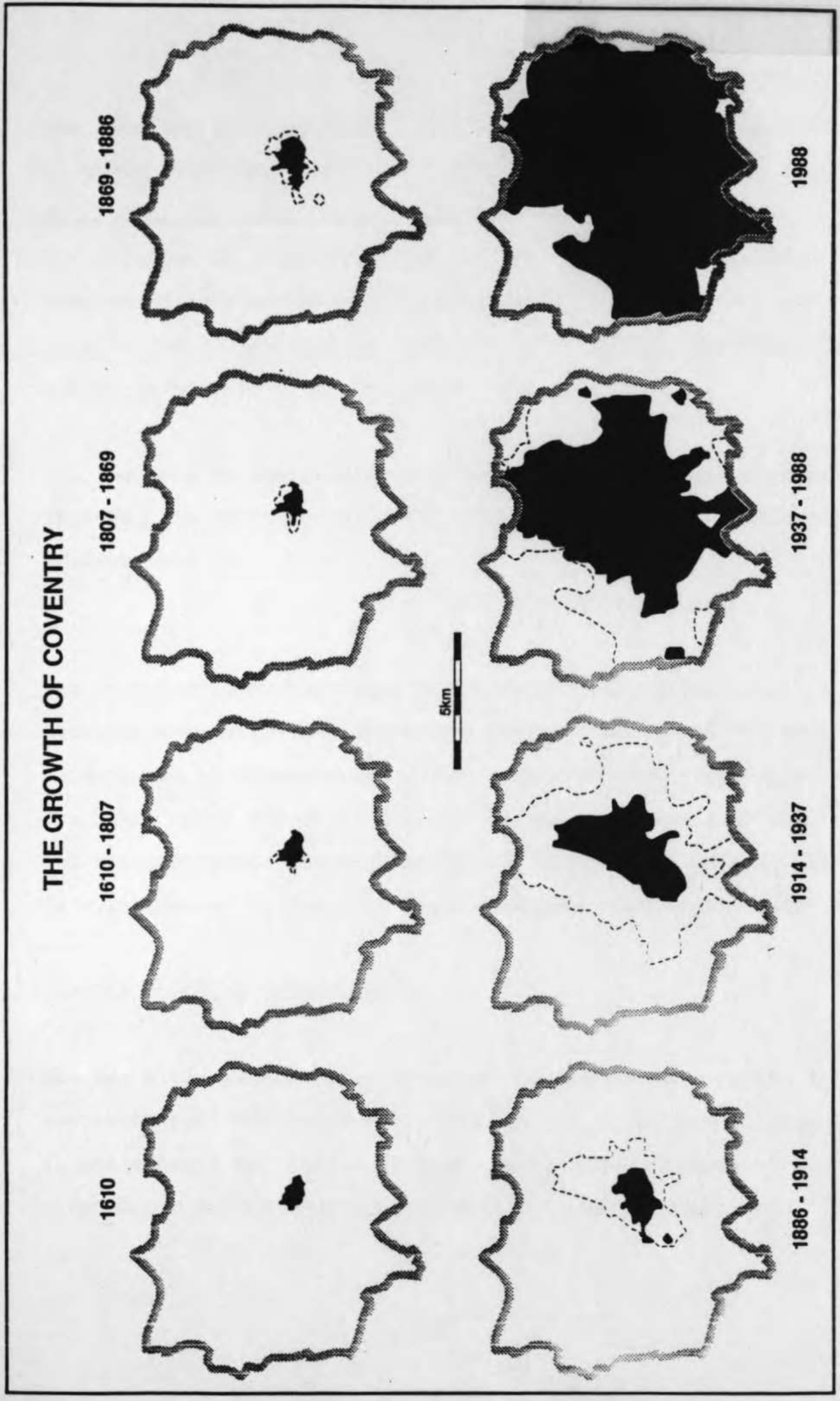
Thus, whilst many authors date the onset of the Industrial Revolution from lake sediment pollution histories as early as 1872 (Batterbee *et al.*, 1988) or even the mid nineteenth century (Oldfield *et al.*, 1983) in fact the Industrial Revolution in Coventry began to make its mark, both in the increase in manufacturing industry as outlined above and in

Fig 3.4 Population of Coventry since the Domesday survey



(after Stephens, 1969 and various others)

Fig 3.5 The growth of Coventry 1610-1807 (P Clarke, pers. comm.)



the increase in population as illustrated in Figs 3.4 and 3.5 in about 1900. The reasons for this were probably due to the decline of the domestic manufacturing industry leaving the City without an industrial base as the Industrial Revolution progressed in other areas. Richardson (1972) emphasises the role of the Common land in Coventry in physically impeding the spread of manufacturing industry:

"As long as the Commons remained, the city's expansion was impeded, one of the reasons why Coventry missed the Industrial Revolution."

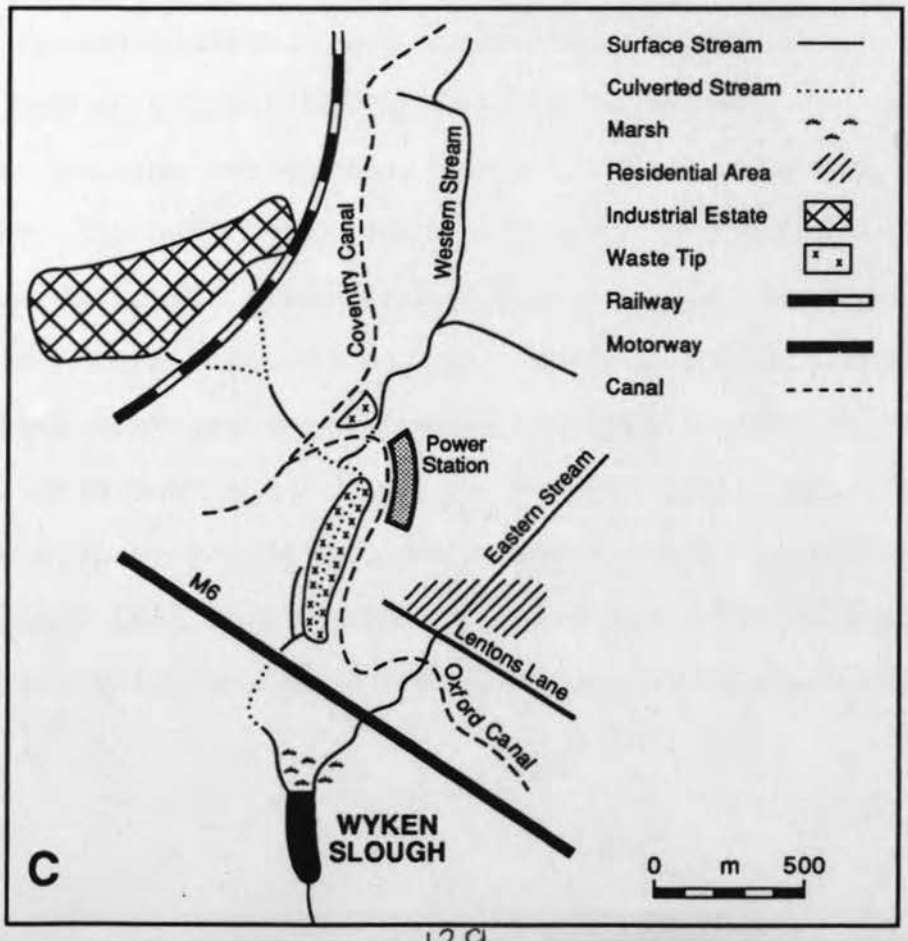
Richardson (1972) p 9.

The increase in contaminants released in association with burgeoning industry and increased urbanisation would therefore be expected to have started later in Coventry than elsewhere. The heavy metal concentrations in the lake sediments of the two research sites would therefore be expected to reflect this late initiation of Coventry into the Industrial Revolution.

3.3 The Research Catchments

The two sites selected for detailed investigation were the Swanswell Pool and Wyken Pool (Fig 3.6). A brief description of the present day lakes and their associated catchments is given below before considering their documented histories.

Fig 3.6 Location of Swanswell and Wyken Pools
a. Coventry
b. Coventry boundaries
c. Wyken Slough catchment



3.3.1. Swanswell Pool

Swanswell Pool is a small freshwater lake (0.73 ha) situated in the centre of the City of Coventry between the old city wall and the mid nineteenth century development of Hillfields (Fig 3.8). Originally a green field site, the lake is now surrounded by a small park (< 1 ha) which effectively forms its surface water catchment. The park in turn is bounded by the Coventry and Warwickshire Hospital, the Stoney Stanton Road and the main West Midlands Passenger Transport Executive (WMPTE) bus depot at Pool Meadow. Fig 3.6 b illustrates how close the Pool is to the City Centre.

The Pool is bounded by concrete coping stones which are surrounded by either paved or metalled pathways. These pathways pass through the grassed areas and out onto public footpaths. The park presently contains mature sycamore trees (*Acer pseudoplatanus)* and willow (*Salix* spp.).

The main inlet to the pool is located in the northeast corner and the outlet to a surface drain is in the southeast corner. The only other source of water for Swanswell Pool in the recent past, apart from the runoff from pathways and direct rainfall input, may have been sporadic leakage from the hospital settling tank located some 50m to the north of the Pool. This source has now been connected directly to the storm drain system, (J. Batty, NRA (Severn Trent Region), pers comm).

There is a small island located near the northern end of the Pool which was occupied by mature trees including Willow

(*Salix* sp.). The island is reinforced by brickwork around the sides. The structure of the island has recently become unstable and several of the trees were lost when the island began to disintegrate. Water birds such as the Mute Swan (*Cygnus olor*), ducks (*Anas platyrhnchos*) and moorhens (*Gallinula chloropus*) nest and raise young successfully both on the island and on the metal cages along the dam wall. The Pool was stocked with Bream (*Abramis brama*) in the past and anglers have been observed catching small live specimens. Dead specimens have also been found, particularly in hot conditions when the water becomes deoxygenated. There is little or no littoral or benthic flora, but there are examples of free-floating vegetation present in the form of algae and pondweed (*Potamogeton* and *Chara* sp). Red *Tubifex* worms and a variety of molluscs represent the invertebrate fauna, although an exhaustive survey of biota has not been carried out at this site and no ecological surveys are known to exist.

3.3.2 Wyken Pool

Wyken Pool is a much larger freshwater feature than Swanswell Pool, being 2.25 ha in area with a surface water catchment of 450 ha. This catchment collects runoff from residential areas as well as from industry, landfill leachates and a water reclamation works. The Pool is surrounded by parkland and permanent pasture which is used for grazing and retains mediaeval ridge and furrow features. Immediately to the north

of the site is an area of marshland designated as a Local Nature Reserve (LNR) in 1990.

The Pool has two major channelled inflows. The Wyken Slough Brook drains the western side of the catchment. Fig 3.6c shows the Brook passing through two landfill sites one of which discharges through a disused water treatment plant, and a major industrial area, the Bayton Road Industrial Estate. The second inflow is referred to here as the Eastern Stream, and drains predominantly agricultural land, although there is some storm drainage from the M6 motorway which was built in 1971, Lentons Lane and Hawksbury Lane. Both streams negotiate the Coventry Canal and pass under the M6 motorway which dominates the northern end of the Pool as is shown in Plate 1. The Wyken Slough Brook passes, via a drainage ditch, into the Pool in the north-western corner. The Eastern Stream drains through the area of marshland and into the Pool. The marshland extends down the eastern side of the Pool as is shown in Fig 2.7b with a finger-like projection about half way down. This marshy ground extends to the outlet.

The public footpath passes W-E to the north of the Pool, the inlets flowing under it enclosed in a pipe in the case of the Eastern Stream, and under a footbridge in the case of Wyken Slough Brook. At the outlet, a footpath passes over a footbridge. Between the footbridge and a controlling overspill weir is an area of marsh which forms an important habitat for swans which have been observed nesting here (see Plate 2). The weir plate was installed to provide a water balance mechanism

Plates 1 and 2

1.(top) Domination of the site by the M6

2.(bottom) Swans nesting at Wyken Pool

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for the downstream River Sowe (R.Ashby, Coventry City Engineers, pers comm).

There are various water fowl on the lake including geese, both Canada (*Branta canadensis*) and common (*Anser sp.*), mute swans (*Cygnus olor*) (Plate 2), Mallard (*Anas platyrhynchos*) and moorhens (*Gallinula chloropus*). Littoral vegetation is present, particularly in marsh areas, which mostly consists of rushes and reeds (*Typha latifolia* and *Phragmites communis*). Tables 3.1 a and b show the results of a recent ecological survey carried out by Ambridge (1989) and a more extensive project undertaken by a local school (Jones 1982) which show the range of fauna living in the Pool.

There are few trees, although Poplar (*Populus* sp) line the footpath to the north with hawthorn (*Crataegus monogyna*) hedges. There appears to be little thriving nekton and local anglers suggested that the Pool was not well stocked with fish. No free-floating plants were seen, although the thick mats of algae found on the lake bottom were unidentifiable due to a covering of organic matter and silt.

Although Wyken Pool may be a settling tank for particulate pollution derived from its catchment, it is still capable of sustaining a range of aquatic life.

Table 3.1 a Fauna at Wyken Pool after Ambridge (1989).

Individuals caught per 5 minute fishing effort

	Site 1	Site 2	Site 3	Site 4	Site 5	Total
*S. complanata**	0	0	3	0	0	3
L. peregra	44	0	11	2	2	59
P. jenkinsii	3	120	6	0	18	147
A. lacustris	0	0	2	0	0	2
WORMS (OLIGOCHAETAE)						
Tubificid[1]	0	0	0	2	0	2
ARTHROPODA (INSECTA)						
ADULT: *Corixa*	33	329	235	0	109	706
LARVAL *Chironomid*	3	0	2	4	0	9
PISCES						
Gasterosteus aculeatus	0	0	29	0	15	44
TOTAL PER SITE	83	449	288	8	144	972

Key to common names

*Segmentina complanata**	-	Flat Ramshorn Snail
Lymnaea peregra	-	Common Wandering Snail
Potamopyrgus jenkinsii	-	Jenkins Spire Shell Snail
Acroloxus lacustris	-	Lake Limpet
Corixa sp	-	Lesser Water Boatman
Chironomid sp	-	Blood Worm Larvae
Gasterosteus aculeatus	-	Nine-spine Stickleback
Tubificid	-	River Worm

For location of sampling stations, see Fig 2.7b

*=*Hippeutis complanatus*

Table 3.1 b Fauna at Wyken Pool

b. After Jones (1982) relative abundance per 5 minute fishing effort.

	Stations							
	1	1b	2	3	4	5	6	7
MOLLUSCA								
a.Gastropoda								
P. planorbis	1	1	3	3	2	2	0	0
P. (carinatus?)	0	0	0	0	1	1	0	0
L. peregra[1]	3	3	3	3	3	3	0	0
L. stagnalis	3	3	3	3	3	3	0	0
G. laevis	0	0	1	1	0	0	0	0
b.Lamellibranchiata								
S. (lacustris?)	2	2	2	2	2	2	0	0
WORMS (OLIGOCHAETAE)								
a.Hirudinaea								
E. octoculata	0	0	0	0	1	2	0	0
b.Oligochaetae								
L. variegatus	0	0	1	0	1	1	1	1
Tubificid[1]	2	4	4	4	1	0	0	0
ARTHROPODA								
a.Copepoda								
C. strenuus			Ubiquitous					
b.Crustacea								
D. pulex			Ubiquitous					
A. (foliacius?)			Ubiquitous					
G. pulex	1	1	1	1	2	2	0	0
A. aquaticus	2	2	2	2	3	3	0	0
c.Insecta - Adult								
Corixa[1]	1	1	0	0	2	4	0	0
Notonecta	1	1	0	0	1	3	0	0
G. (natator?)	2	2	0	0	2	2	0	0
L. hyalinus	1	1	0	0	1	1	0	0
d. Larval								
B. (rhodani?)	0	0	1	1	1	1	0	0
Chironomus	0	0	4	4	3	0	0	0
Perla	0	0	0	0	0	1	0	0

[1] see Table 3.1a, others see key next page

Key to Table 3.1 b

Planorbis planorbis	The Ramshorn
Planorbis (carinatus?)	Keeled Ramshorn
Lymnaea stagnalis	Great Pond Snail
Gyraulus laevis	Smooth Ramshorn
Sphaerium lacustre	Pea Mussel
Erpobdella octoculata	Leech
Lumbriculus variegatus	Segmented Bristle Worm
Cyclops strenuus	Water Flea
Daphnia pulex	Common Water Flea
Argulus (foliacius?)	Fish Louse
Gammarus pulex	Freshwater Shrimp
Asellus aquaticus	Water Louse
Notonecta	Water Boatman
Gyrinus (natator?)	Whirligig Beetle
Laccophilus hyalinus	Diving Beetle
Baëtis (rhodani?)	Mayfly Nymph
Perla	Stonefly

3.4 Site histories

3.4.1 Swanswell Pool.

The complete history of Swanswell Pool from its probable construction as a medieval fishpond associated with Coventry Priory is detailed in Charlesworth (1990). The history of the Pool up to about 1800 is summarised in Table 3.2 and the five maps in Figs 3.7 & 3.8 a - d illustrate the changing nature and land use of the environs of the Pool.

John Speede's map of 1610 (Fig 3.7) shows the Pool without inlets, but with two outlets, and serves to illustrate how the Pool was situated originally outside the boundary of the City of Coventry. Thomas Sharps' map of Coventry (1807) shows Swanswell Pool with the much smaller New Pool to the southwest (Fig 3.8 a). There is no inlet shown on this map, although one is shown on later maps, so this omission may have been a cartographic oversight. There are allotments or ornamental gardens around the Pool with many trees, and pasture land divided into fields by hedges. The outlet appears to have been used for irrigation.

By 1828, New Town was laid out in the Hillfields area and eight streets to the east of Swanswell Pool were constructed. The map of 1837 (Fig 3.8 b) shows the building of New Town and warehouses and streets are also shown. The Springfield Brook, feeding Swanswell Pool is shown meandering through the countryside.

Fig 3.7 John Speedes's 1610 map "The ground plott of Coventre"

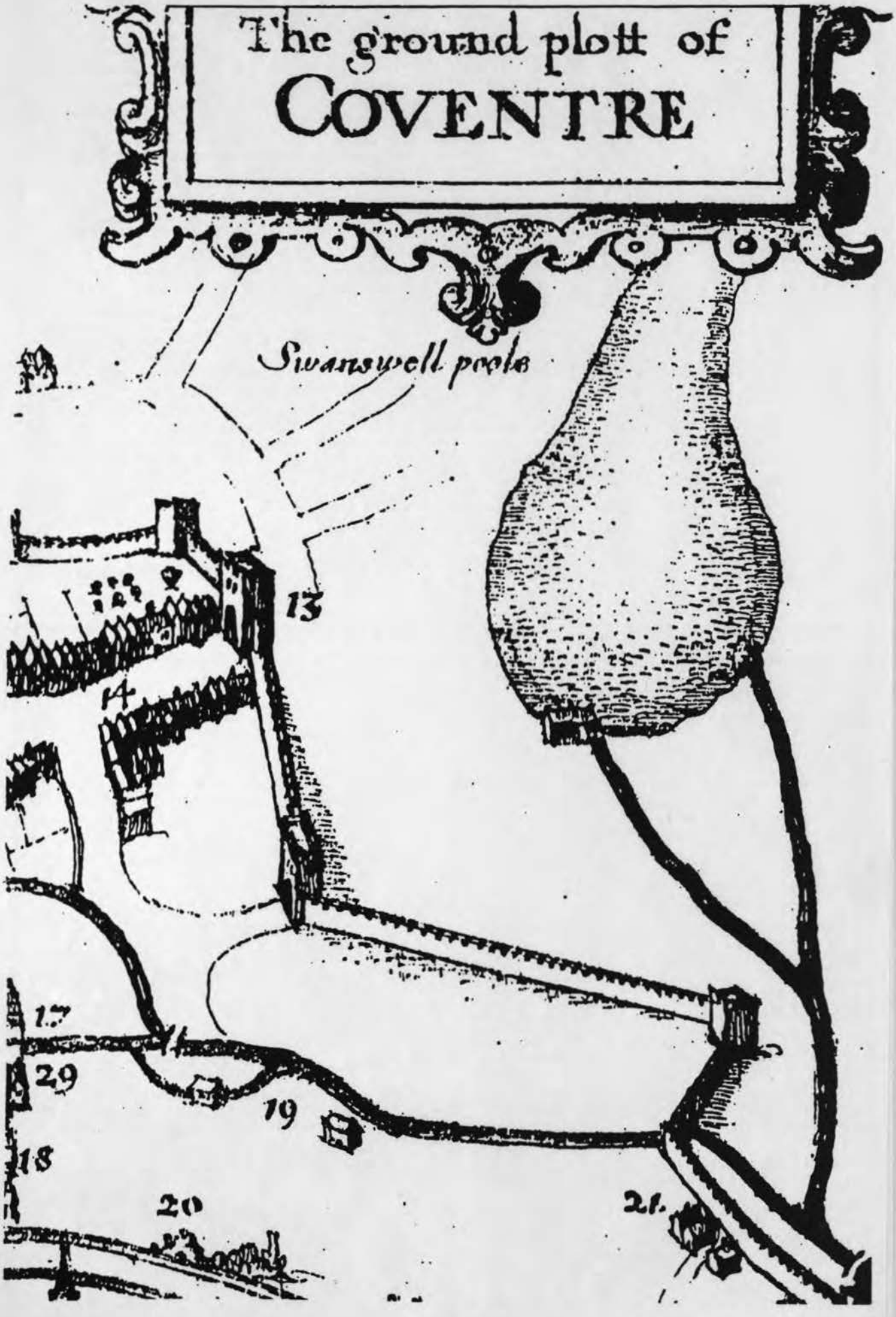


Fig 3.8 Historical maps of pre-20th century central Coventry

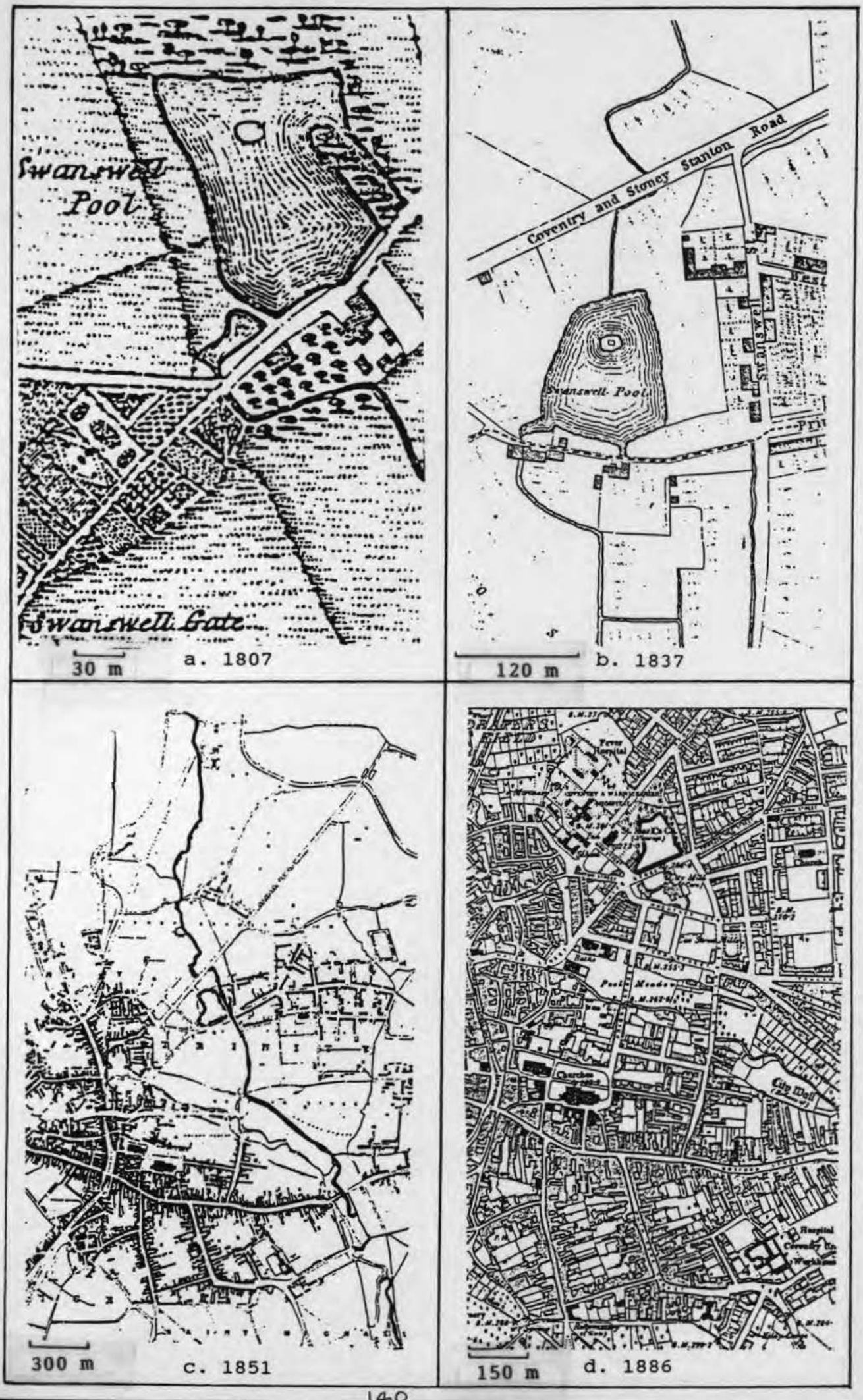


Table 3.2 Swanswell Pool history to 1800. (After Charlesworth, 1990)

Year (AD)	Event / Evidence
pre 1000	No evidence of pre-Roman settlement in Coventry "Coventry" from Anglo Saxon "Cufa's Tree"
1000	St Osburg's nunnery founded
1016	St Osburg's nunnery sacked by the Danes
1043	Foundation of Benedictine monastery by Leofric and Godiva.
1066	Coventry not mentioned in Domesday although the area belonging to Godiva is described.
1162-74 or 1177-81	Charter of Earl Hugh of Chester does not mention the existence of Swanswell Pool
1265 +/-90	Possible formation of Swanswell Pool by damming of the Endermere Brook
1355	Tripartite Indenture of Edward III : first mention of Swanswell Pool by name
1411	J Lancaster (1974) represents Swanswell Pool with the Priory's Mill and Orchard.
1425	St. John's Hospital land lay between Swanswell Pool and the sity wall.
1439	Master of St John's Hospital had the pasture below Swanswell Pool.
1480	Prior Deram complained to the Court Leet regarding the townspeople washing in the Pool
1540	Crown lease of Swanswell Pool and New Pool to Henry Over
1545	Swanswell Pool granted to John Hales after the Dissolution
1551	Grant of Swanswell Pool and New Pool to Coventry Corporation
1579	Priors Orchard Mill and New Mill in existence
1610	John Speed's map, the forst cartographic representation of Swanswell Pool, shows the Pool as pear-shaped, no inlets but with 2 outlets. Situated outside the city wall in open countryside. The island is not shown.
1632	Construction of Swanswell Waterworks
1646	Bewley family took a 200 year lease on the Swanswell Waterworks.
1709	Thomas Bewley (Mayor of Coventry) may have owned Swanswell Pool.
1748-9	Samuel Bradford's map shows the Pool divided into Swanswell and New Pools with a spur of land projecting northwards into the Pool. 2 outlets and 2 inlets. The island is not shown, the Pool is surrounded by pasture.

After 1848, an estate of houses was built to the south of Swanswell Pool and New Pool was infilled to make way for White Street. The Ordnance Survey map of 1851 (Fig 3.8 c) shows Swanswell Pool surrounded by streets, with New Town now considerably larger and Swanswell Pool truncated at its southern end with the loss of New Pool. Springfield Brook is shown running to the east of the Pool, in pipes or open conduits; the Pool relying on local springs for its water supply.

The water supply to the citizens of Coventry in the seventeenth century depended to a great extent on springs in the Swanswell Pool area. However, by 1843, only 280 of the 7000 houses in the City were being supplied by the Swanswell Waterworks and, following the 1844 Coventry Water Act, the supply was taken over by new works at Spon End.

The Ordnance Survey map of 1886 (see Fig 3.8 d) shows Swanswell Pool virtually as it is today, surrounded by housing, industry (the "City Mill (corn)" is shown to the south) and the Coventry and Warwickshire hospital to the north. No inlets or outlets are shown.

Correspondance in the local newspapers during October 1988 (Coventry Evening Telegraph), suggested that the Pool suffered bomb damage during the Second World War and needed repairs to stop leakages, although no firm documentary evidence has been found to support this suggestion. There is evidence of the severe damage suffered by the hospital during air raids, and it would seem possible that the Pool was hit by bombs:

"All around the hospital grounds glowed literally hundreds of incendiary bombs.."

Longmate (1976) p 91

Urban development continued around the Pool and in 1946, (source and type unknown) following a series of pollution events, the Hospital spring feeders which maintained the level of water in the Pool after 1850 were cut off and a metered water supply was used (NRA (Severn Trent Region) pers comm). In the mid 1960's, a larger dimension inflow pipe was installed to feed ornamental fountains and hence the metered water consumption was increased.

In 1949, the City Corn Mill occupied the site where the West Midlands Passenger Transport Executive (WMPTE) bus depot now stands. This Mill abstracted 50,000 gallons of water per day from the Pool, which was returned directly to the Pool after use.

A new block was added to the hospital in the 1950's and surface water sewers laid originally to link up with the various sumps and wells to supply the Pool were diverted into the Springfield Brook (NRA (Severn Trent Region), pers comm). The Brook itself was culverted in the 1960's, approximately 2 m below the present-day surface of the Pool.

In recent years there have been periodic spillages from the underground hospital settling tank (a 2 m deep storage reservoir) with high ammoniacal nitrogen and BOD. The surface water sewer taking outflow from the hospital flowed directly

into the Pool from the north. Severn Trent Water Authority have diverted this source of pollution into the nearest surface sewer system.

The Pool has, therefore, undergone wide ranging changes to its catchment, starting with agriculture and pasture and latterly with 140 years of urbanisation and industrialisation.

3.4.2. Wyken Pool

The development of Wyken Pool, in contrast to Swanswell Pool, is poorly documented. Evidence suggests that it formed after mining subsidence in about 1850 (Coventry City Council, pers comm). Cartographic evidence presented in Fig 3.9 a shows "Marcher Brooke" flowing where Wyken Pool is now on the Ordnance Survey map surveyed in 1835. The Second Edition Ordnance Survey was produced in 1883 (Fig 3.9 b) and clearly shows the Pool to the south of Aldermans Green with Wyken Colliery to the east.

In 1850 there were two main collieries in the area. Hawksbury Colliery (now been renamed Main Pit Farm) and Victoria Colliery (Stephens, 1969).

Victoria Colliery was permanently closed after a series of fires in the workings in 1870. All mines in the area have been disused since 1886 and only old shafts and workings are left. A map of the Wyken Colliery dated 1905 in the Coventry Record Office (CRO), shows mining to the east of the site, most of which was from the Ell and Ryder seams. These seams appear to

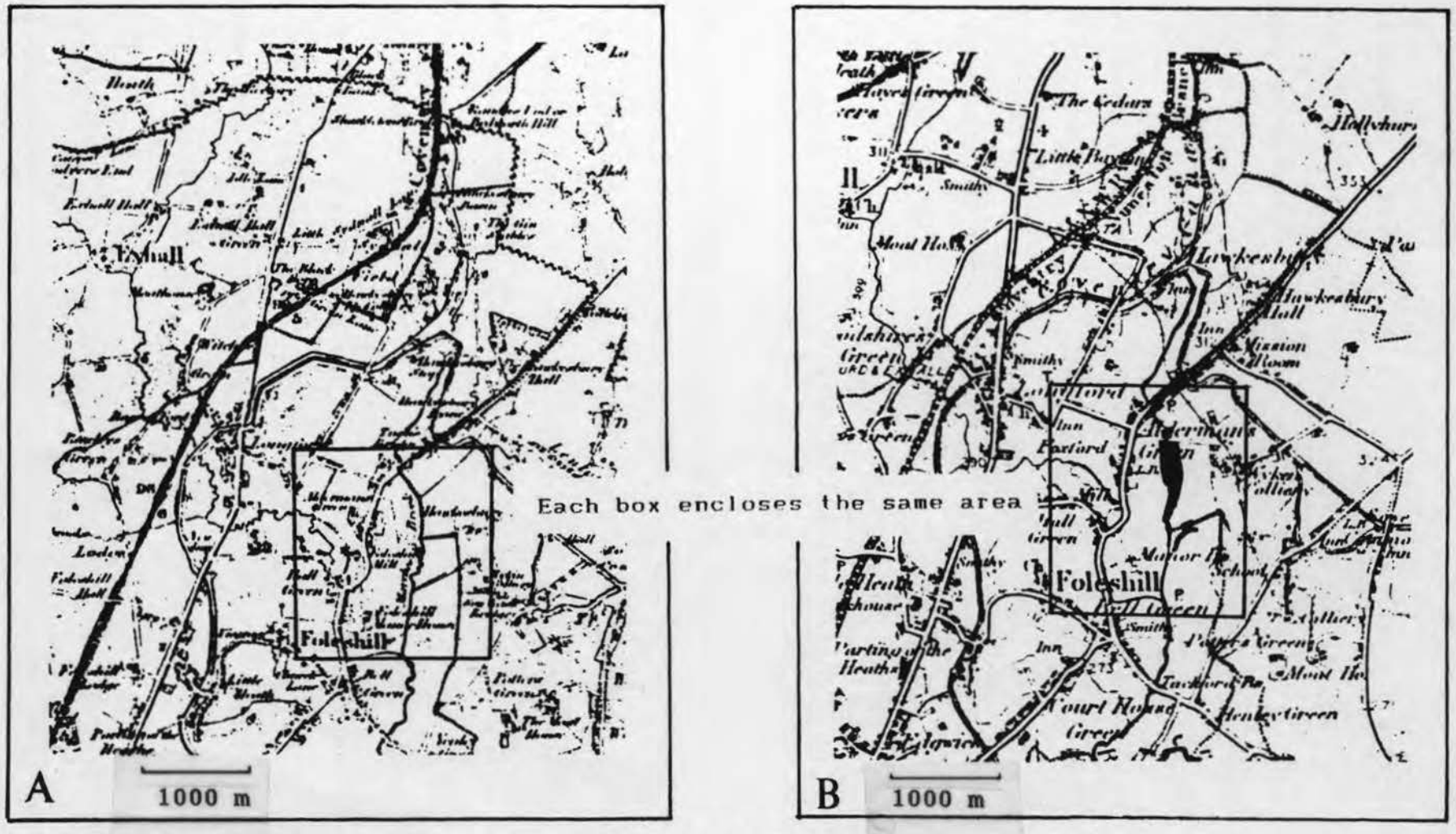


Fig 3.9 Historical maps of pre-20th century Coventry, Alderman's Green
a. 1835
b. 1883

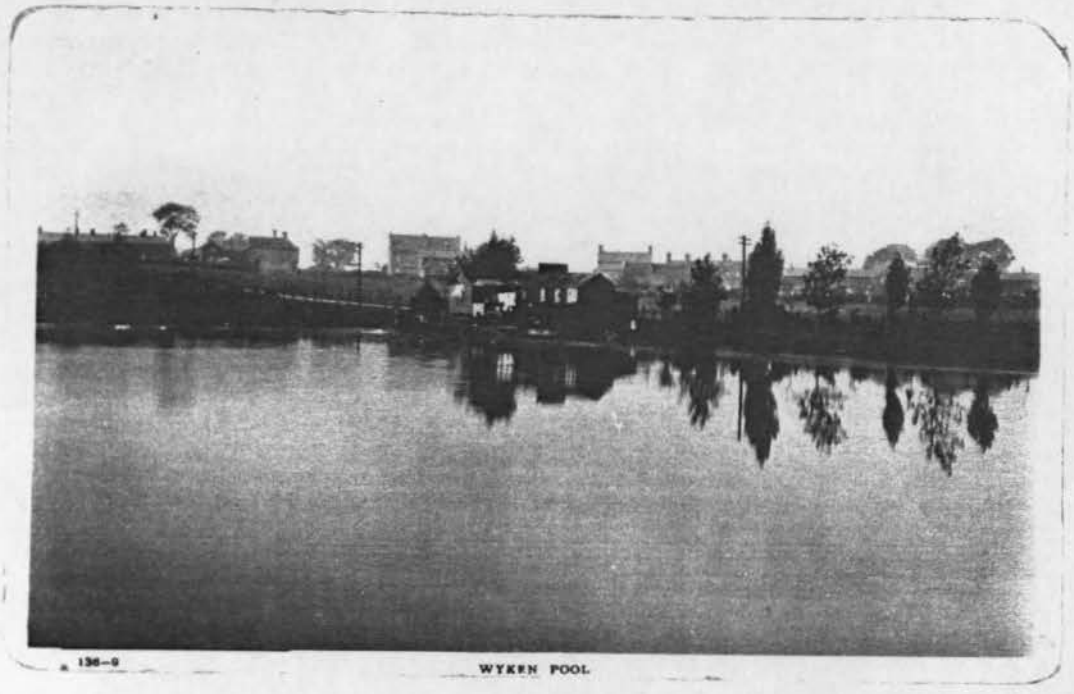
have been worked out between 1845 and 1881. Other dates appear around the site of the Pool itself (1864, 1872, 1881) and presumably refer to active mining beneath the site. Notes from the Geological Survey by Howell (1855/6), and lodged in the (pers. comm. British Geological Society, 1993) Geological Survey record office do not mention the Pool and, as the base map for the survey was produced in 1835, this does not show the Pool either. Enquiries at the British Coal record Office also failed to produce any evidence which might tie the date of formation of Wyken Pool more closely than between the dates of the two Ordnance Surveys.

Industrial Growth and development in the Wyken Catchment.

Ribbon weaving remained the main industry in the Foleshill area of Coventry until 1860. There were 300 power looms there in 1866, although by then most were idle. Since the First World War, most firms centered on Foleshill were concerned with engineering, textiles and the construction industry.

Photographic evidence of the Wyken Pool was obtained from the boatmans family, who lived there in the 1920's and 30's, and are presented in Plates 3 to 6. Williams (1993) interviewed the family who gave evidence for the existence of two islands in the Pool on which the boats used to be tied (Fig 3.10).

Newspaper articles (Coventry Evening Telegraph) from 1958 indicate the decline in quality of the Pool. On November 21,



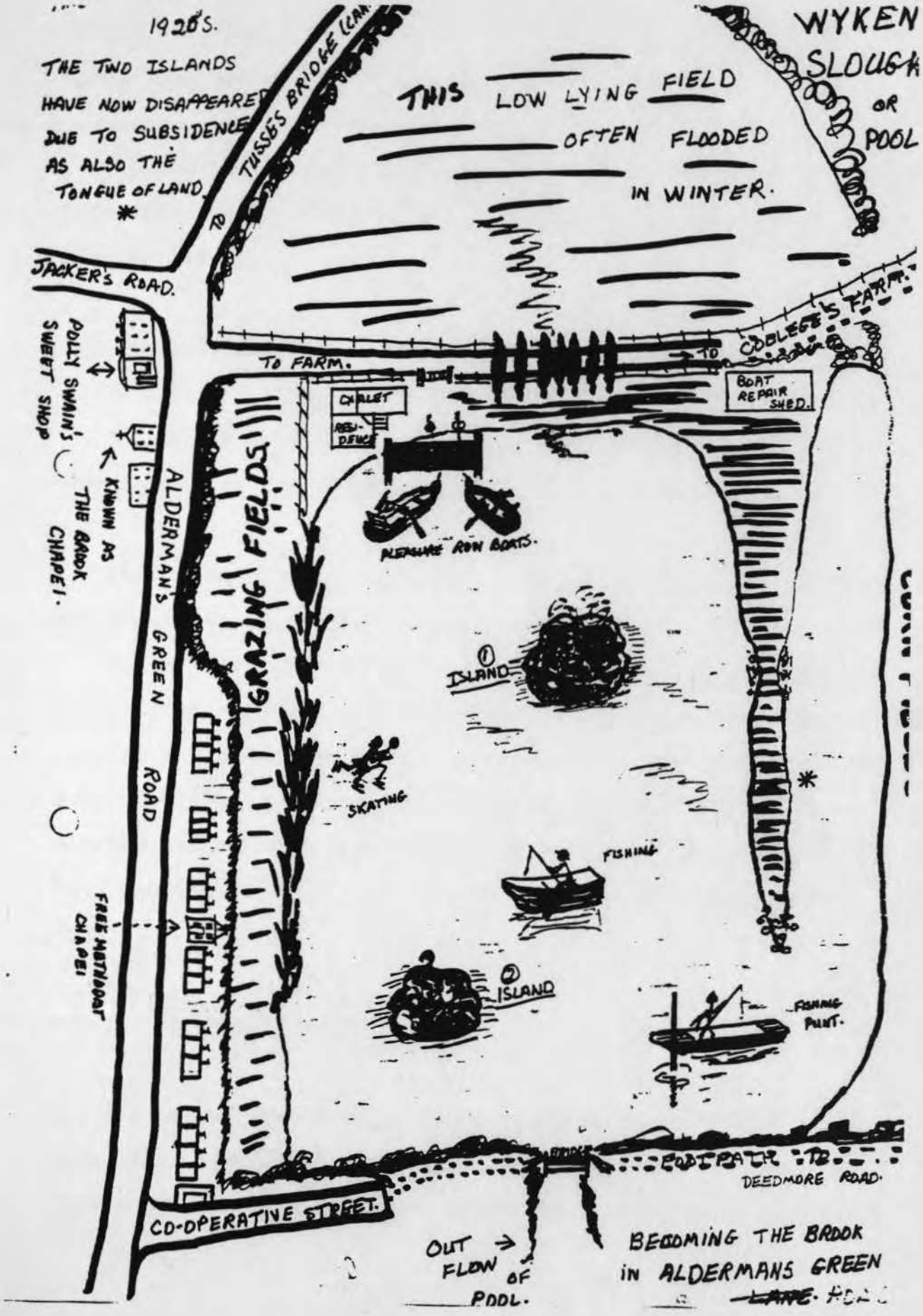
Plates 3 and 4 Wyken Pool in the 1920's

3. (top) The Pool and boatman's house

4. (bottom) The boatman fishing on the Pool

Plates 5 and 6 Wyken Pool in the 1920's: boating on the Pool

Fig 3.10 Map drawn by surviving boatman's family of Wyken Pool in the 1920's (Williams, 1993)



1958, 1000 fish, mainly roach and bream, were killed, when Wyken Pool was polluted..

"..the fish were being poisoned by a discharge of industrial waste, carried by a stream which flows into the Slough (*sic*)."

The same source, in September 1968, reported that

"..many fish were killed in July this year.." and that "the source of the pollution has not been disclosed"

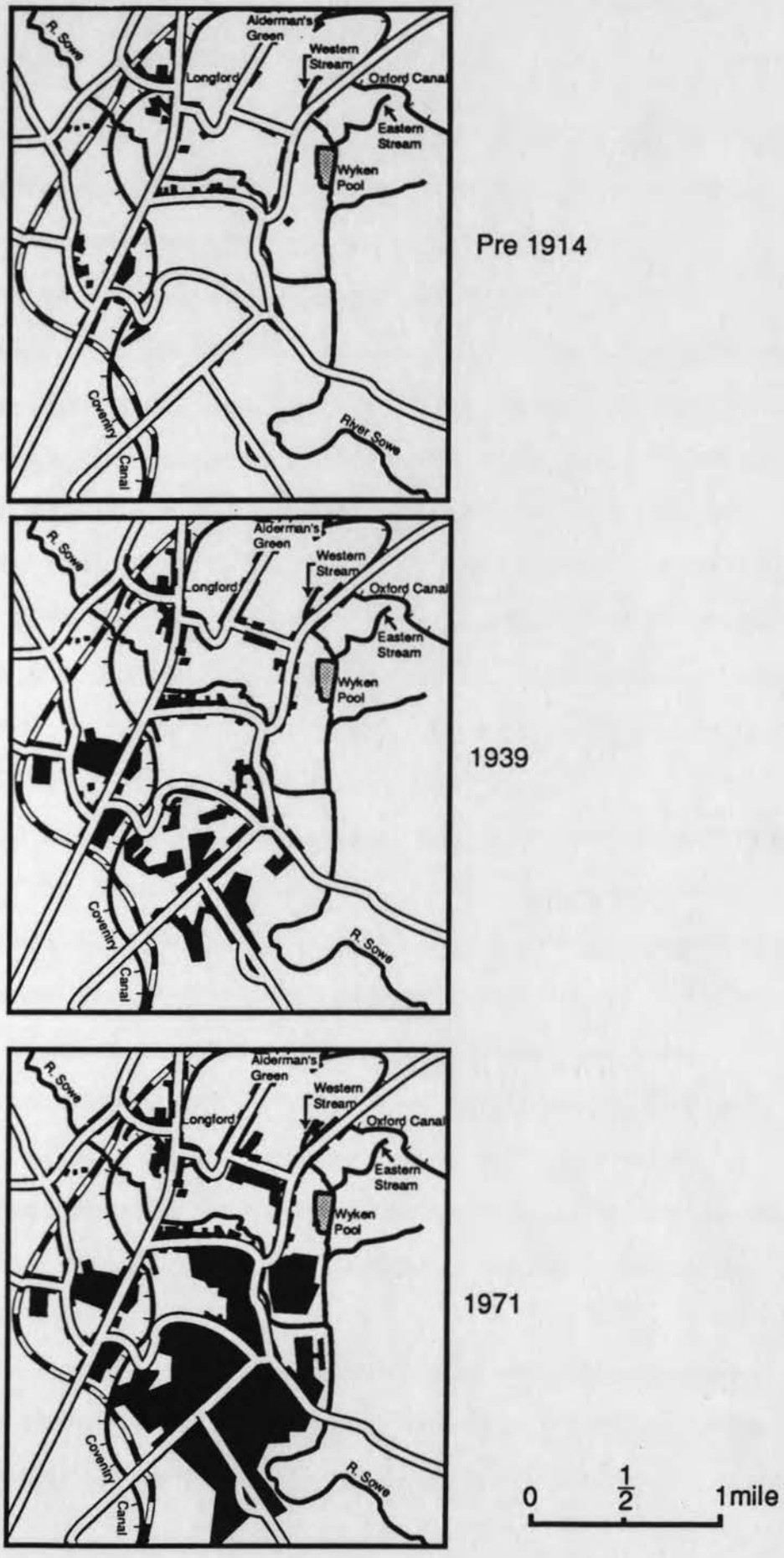
but it was thought that flooding in the catchment carried the pollution to the Pool.

Wyken Brook was canalised in 1975 to improve drainage due to problems with the area flooding periodically and presumably causing the pollution events outlined above. At the same time, some dredging of the southern edge of the lake margins were carried out although little disturbance of the majority of the lake bed occurred (R. Ashby, Coventry City Engineers, pers comm).

3.4.3. The Wyken Slough Catchment.

Fig 3.11 shows the development of housing in the Longford area. This area is to the north of Coventry and includes the catchment area of Wyken Pool. Large housing estates were built

Fig 3.11 The Longford area, housing development pre-1914 to 1971.



during the 1950's and 60's, mainly to the south of Wyken Pool, but the Longford area was also subject to extensive building programmes (Coventry Geographical Association, 1971).

The historical aspects of a landfill site at Hawksbury are confidential and no records exist of what was dumped there prior to 1974 when the Control of Pollution Act 1974 (now superceded by the Environmental Protection Act 1990, Part II) required disposal records to be maintained of all chemicals disposed of in this way. Unfortunately, there are also no records from 1974 as the tenure of a succession of new owners was too short for the legislation to be enforced. However, the site is subject to flooding and hence any pollutants it may contain could be moved downstream by flood water.

The Bayton Road Industrial Estate was built in about 1969 on the site of an abandoned colliery (J. Batty, STWA, pers comm) and at one time "bright" processing (ie the cleaning of copper and brass with nitric and sulphuric acids) as well as zinc-cadmium battery manufacture occurred there. Part of Bayton Road was sewered until 1988 by a pumped system. This periodically failed, leading to contamination of surface waters with foul sewage. Improved sewerage has been installed adjacent to the Wyken Brook and its lower reaches, close to the marsh.

The Power Station site, including land on the opposite side of the canal, has been used for non-toxic landfill. The first Waste Disposal License was issued in 1984, but the site

has been inactive since 1990 (Environmental Health, Coventry City Council, pers. comm.)

By 1981, the "Coventry Evening Telegraph" carried reports of volunteers needed to help clear the Pool of rubbish..

"..the Slough (*sic*)..was popular for boating, fishing and rambling. But the water has become polluted, the land is used as an unofficial tip and buildings have been badly vandalised."

Two skips of rubbish were removed from the site by the volunteers. The Friends of Wyken Slough were formed in 1982, but their hut was gutted by fire in 1986 and removed in 1990.

The marsh to the south of the Pool was designated a Site of Importance for Nature Conservation (SINC) in 1977. Unlike Sites of Special Scientific Interest (SSSI), SINCs do not have any legal standing. On September 12 1990, Coventry City Council declared the site a LNR.

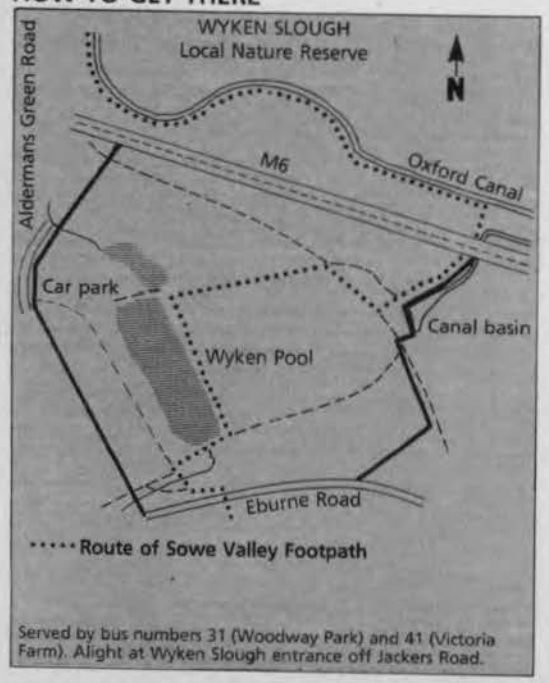
Wyken Pool and the land around it, known collectively as "Wyken Slough" (Slough= marsh) is to be incorporated into an 11 mile "green ribbon" walk through Coventry (Fig 3.12), which may herald a brighter future for the site.

Table 3.3 summarises the major changes to both lake basins in the last 140 years and illustrates the increasing urbanisation and industrialisation taking place around them.

Table 3.3 Major changes to Swanswell and Wyken Pools from 1850

Date	Swanswell Pool	Date	Wyken Pool
1850	Springfield Brook diverted to the east of Swanswell Pool	1850	Subsidence of marshy ground under Marcher Brook
1940-45	Possible bomb damage during the Second World War	1886	closure of mining activities around the Pool
1946	Hospital spring feeders cut off and metered water supply installed	1920-30	2 island used to tie boats up
1949-50	Buiding of the WMPTE bus depot, Pool Meadow	1958-68	Local newspaper articles on the declining conditions at Wyken Pool
1950	New hospital block built to the west of Swanswell Pool	1969	Construction of Bayton Road Industrial estate
1960's	Culverting of Springfield Brook 2 m below present Pool surface	1971	M6 built
		1977	Marsh designated a SINC
		1990	Site designated a LNR

HOW TO GET THERE



Served by bus numbers 31 (Woodway Park) and 41 (Victoria Farm). Alight at Wyken Slough entrance off Jackers Road.

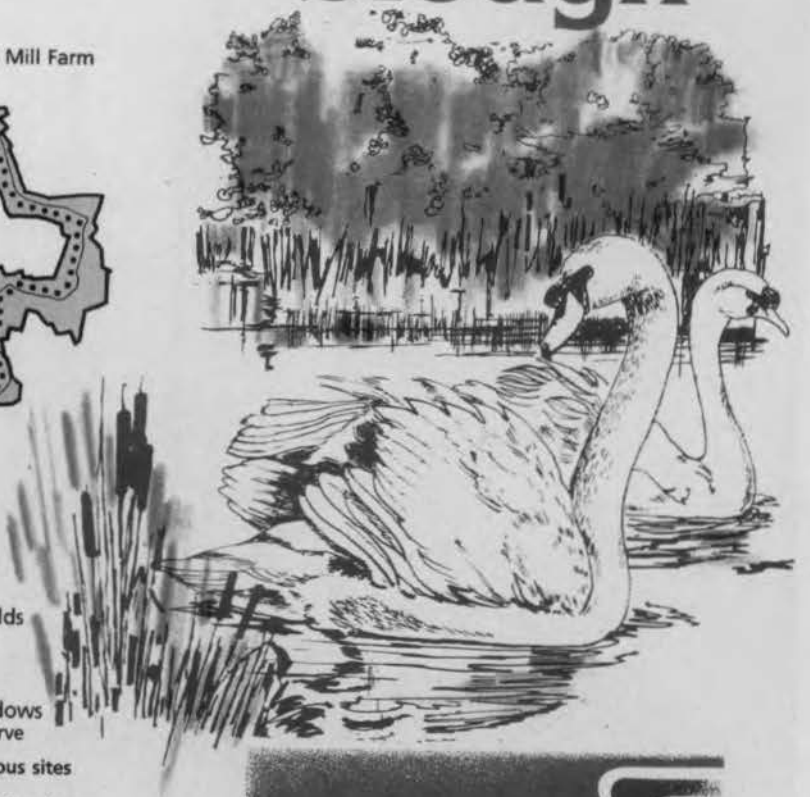
Wyken Pool is the largest expanse of water in Coventry and is an obvious attraction for wildfowl. The rough grassland, scrub and marsh near the Pool also supports a rich variety of wildlife. From Wyken Slough, you can walk under the motorway to the banks of the Oxford Canal and Hawkesbury Junction Conservation Area. The canal towpath forms part of the new Centenary Way Long Distance Footpath, which runs from Kingsbury Water Park and finishes at Meon Hill near Stratford.

The Sowe Valley is an area of Green Belt open space which follows part of the course of the River Sowe for about eight miles. The Valley runs from Hawkesbury Junction Conservation Area in the north, to Stonebridge Meadows Local Nature Reserve in the south.

The Valley links Coventry with the countryside and is particularly important for landscape, amenity, outdoor recreation, local history, education and nature conservation.

A guide to

Wyken Slough



Other Leaflets on the Sowe Valley and various sites of interest are available from the:
Department of Economic Development and Planning,
Strategic & Local Planning Division
Much Park Street, Coventry CV1 2PY.
Telephone (0203) 831292.

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City of Coventry

SOWE VALLEY

Fig 3.12 Coventry Leisure Services produced map of the "green ribbon" walk through Coventry incorporating Wyken Slough

Chapter 4

The Swanswell Pool

4.1 Introduction

This chapter describes the results of field surveys and analyses carried out on the water and sediment samples collected from Swanswell Pool and listed in Table 2.21. The following data are considered first :

1. Following descriptions of the bathymetry and sediment thickness of the lake, are classifications of the lake sediment type and its macrofossil content (Chapter 4.1.2), sediment density and organic matter content (Chapter 4.1.3).

2. The chemical analysis of the lake sediments is divided into two sections: phosphorus and heavy metal concentrations. The latter is further subdivided into a discussion of the spatial distribution of the metals in the surface lake sediments and, in four cores, their change in concentration with sediment depth. Two cores were analysed to chemically fractionate the sediments which would enable the sites of attachment of the heavy metals within the sediment to be assessed (Chapter 4.2.4).

3. Mineral magnetic, radioisotope and particle size analyses complete the description of the physical parameters and are presented in Chapters 4.5 to 4.7.

4. Statistical analysis of the data is presented in section 4.3. This was primarily used to establish whether any relationship existed between individual parameters, but also to assess the usefulness of some of the measurements that were made for the purposes of environmental reconstruction.

5. A consideration of the Swanswell Pool lake sediments is completed by an examination of the molluscan content of a sediment core from Swanswell Pool.

6. Water quality is considered in section 4.5. Measurements were made *in situ*, and in the laboratory. NRA (Severn Trent Region) data are also discussed.

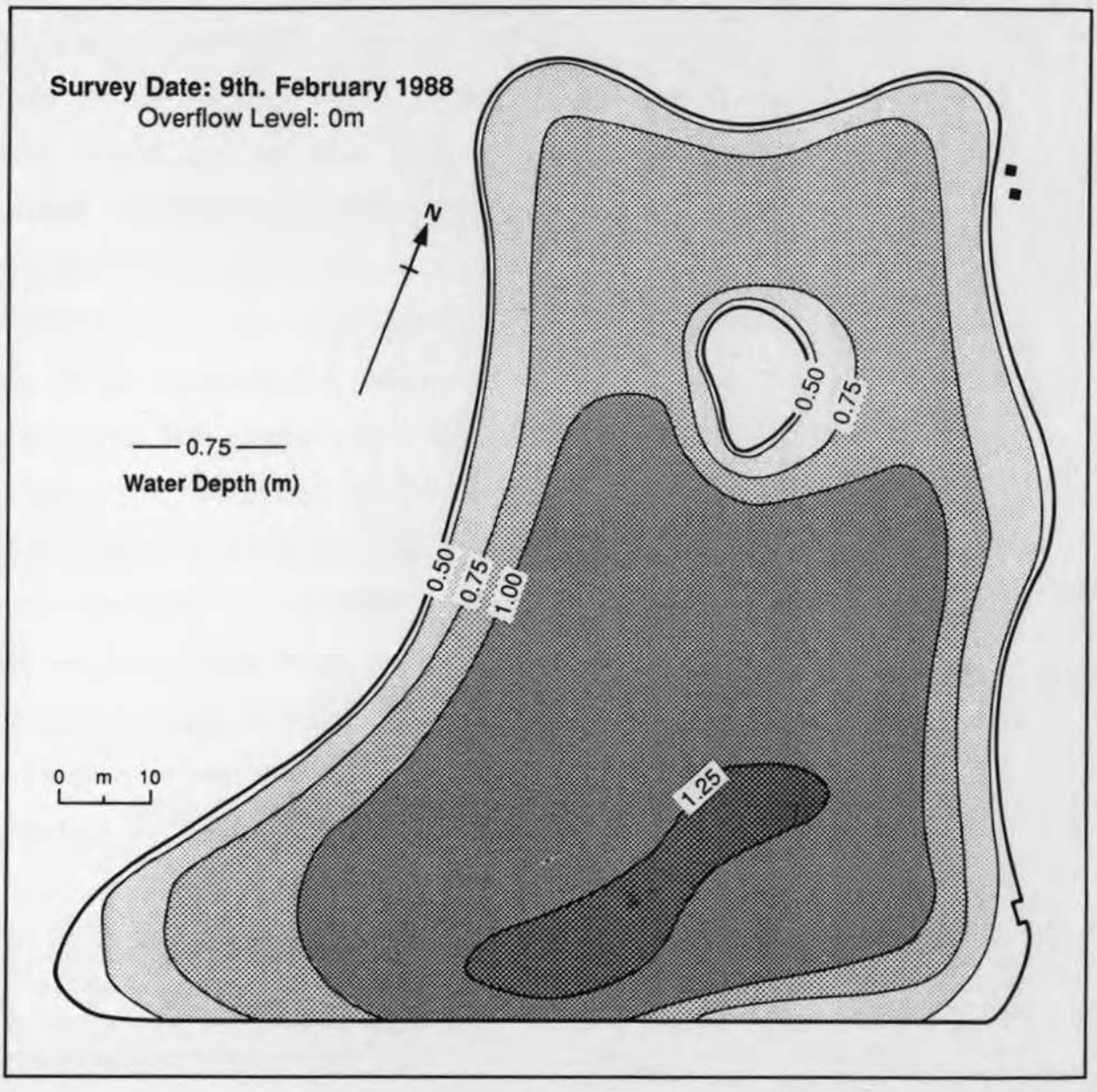
4.2 Characteristics of Swanswell Pool and its sediments

The results of analyses used to reconstruct the pollution history of Swanswell Pool are presented in this section. These include the bathymetry of the lake basin as well as physical and chemical analyses of the sediments deposited within it. Physical characteristic, such as visible stratigraphy, fossils and bulk density, all provide a means to correlate synchronous horizons across the lake.

4.2.1 Bathymetry and sediment thicknesses.

A bathymetric map, based on hand line depth measurements, is given in Figure 4.1. The maximum depth of water, 1.4 m, was recorded in the southeastern corner of the Pool. Over the rest

Fig 4.1 Bathymetry of Swanswell Pool



of the Pool water depths varied between 0.5 and 0.75 m. At the time of sampling there was no head of water over the overspill weir located in the south-east corner of the Pool. Water depths are reported to the level of the weir plate.

Sediment thicknesses were measured by probing with survey rods at intersections of the coring grid (Fig 2.10 a) and plotted by hand. The results of this analysis are given in the form of an isopach map in Figure 4.2. The thickest sediment, over 2.5 m, is located in the central third of the Pool. The island appears to interrupt the general pattern of sedimentation and, on its western side, the sediment is between 2 and 2.5 m thick. The sediment gradually reduces in thickness towards the edges of the Pool, but is truncated to the north and south where the isopachs are much more closely spaced. To the south of the Pool, adjacent to the dam wall, the 1 and 2 m isopach lines converge at the wall, suggesting that the wall was constructed over the original southern end of the Pool (see Figs 3.7 and 3.8). The isopach lines therefore indicate that Swanswell Pool was larger in the past, a factor reinforced by the documentary evidence presented in Chapter 3.

4.2.2 Core stratigraphies

The stratigraphies for the sediment cores retrieved from Swanswell Pool are shown in Figure 4.3, and the macrofossil record is shown in Figure 4.4.

From Fig 4.3, it is possible to provide a general stratigraphic description for the lake sediments using Munsell

Fig 4.2 Sediment thickness

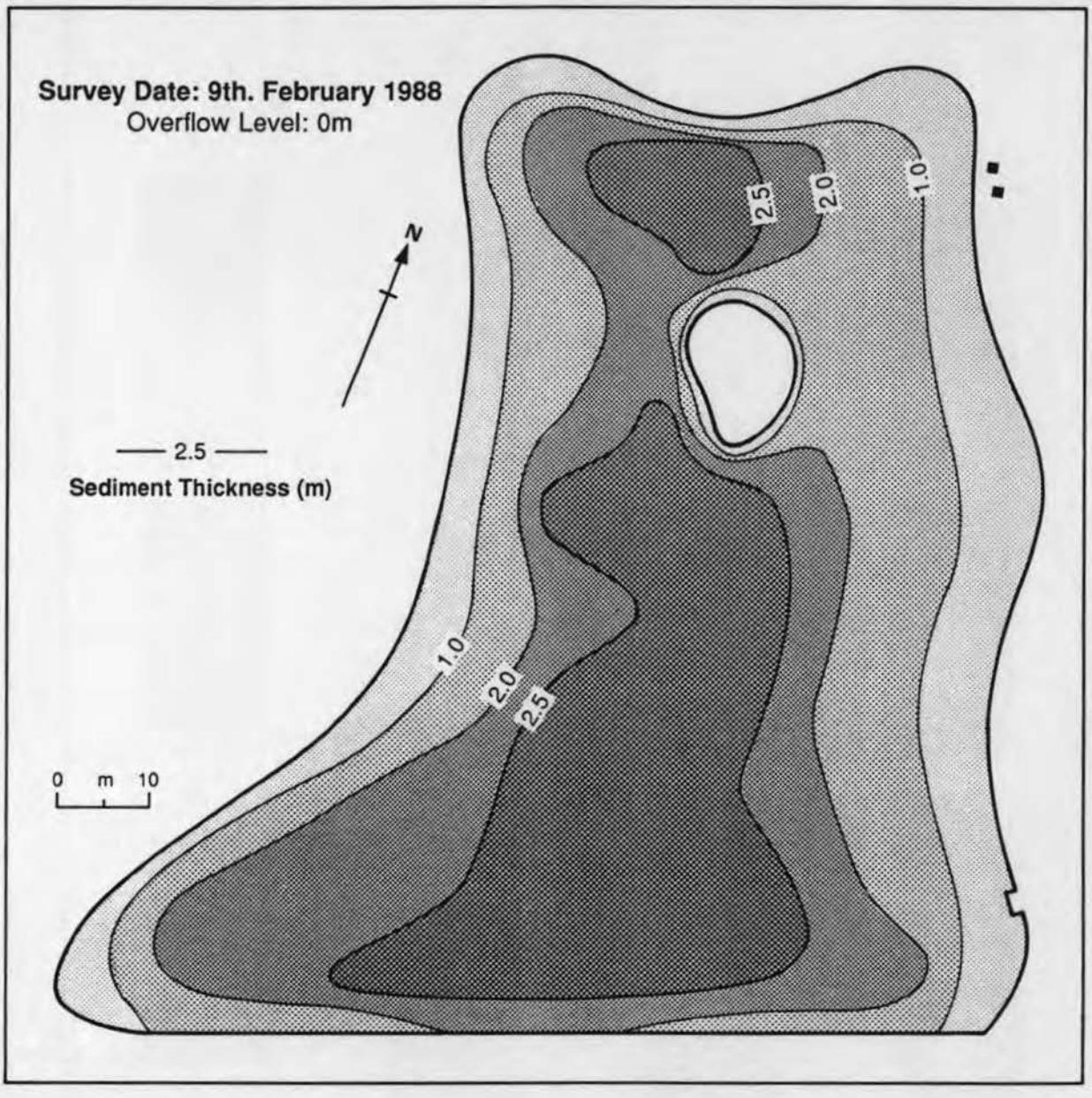


Fig 4.3 Lake sediment type at Swanswell Pool

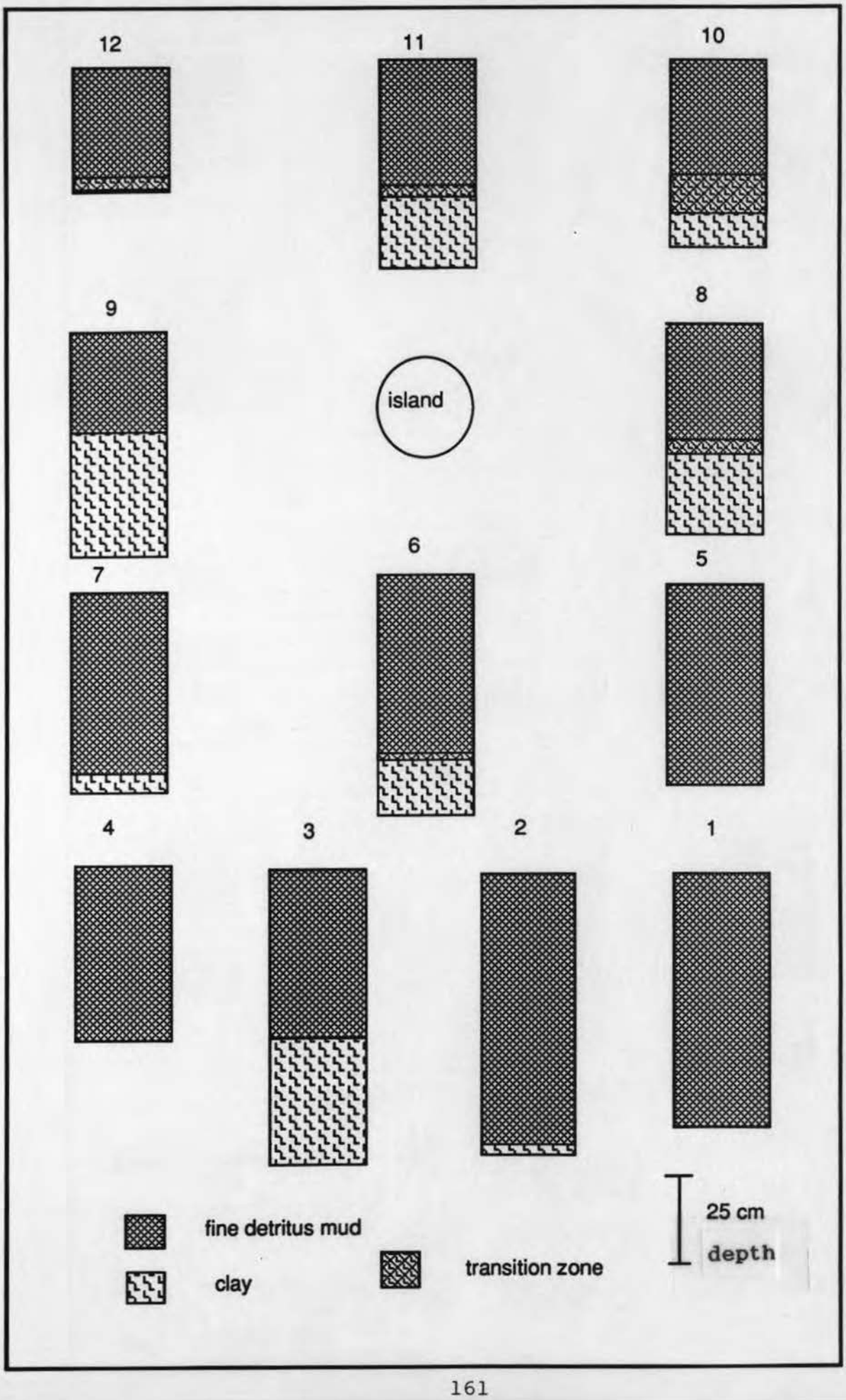
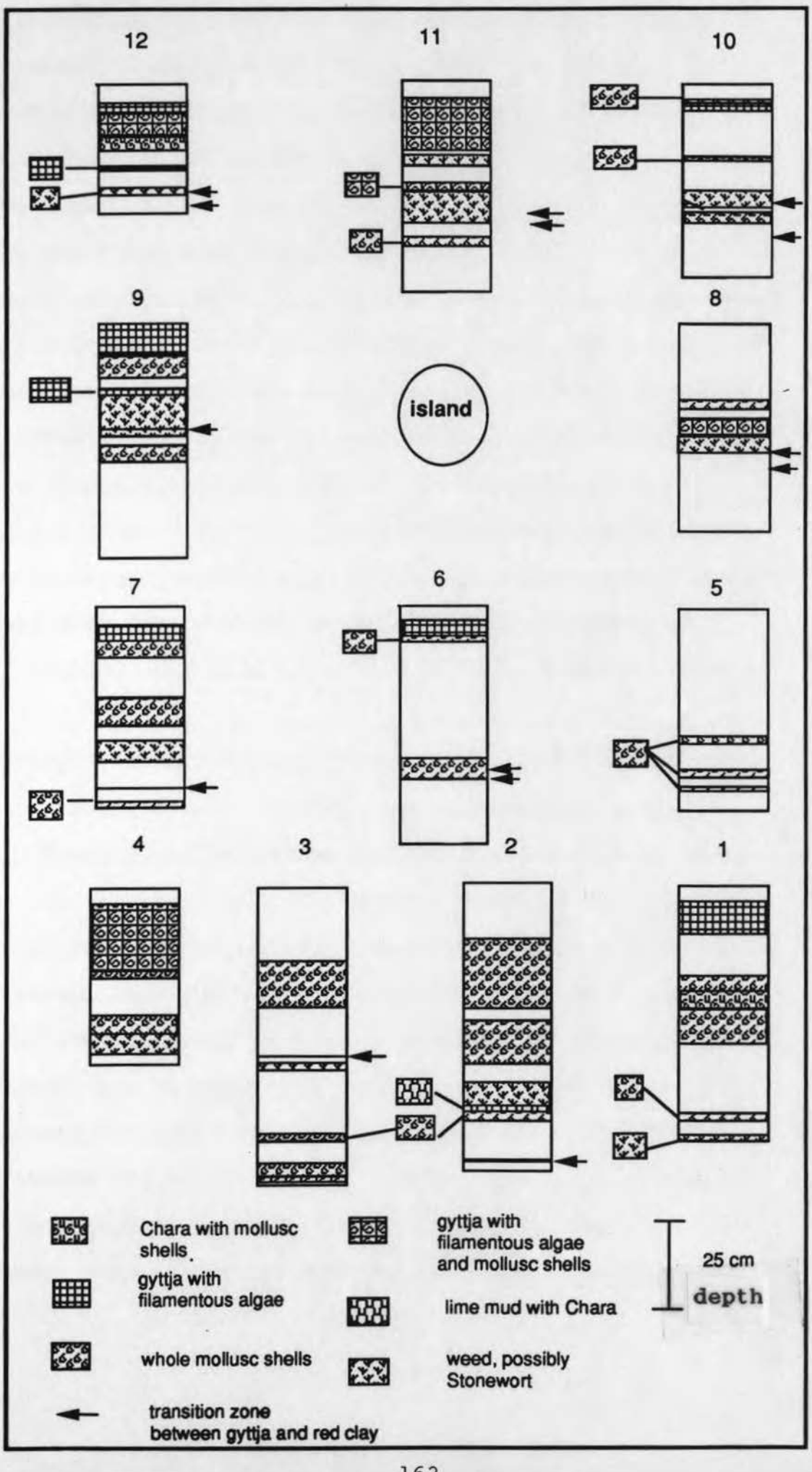


Fig 4.4 Macrofossils in the sediments from Swanswell Pool (based on the Troels-Smith (1955) classification scheme)



Charts (1975) for the colours. The upper sediments were a uniform black to grey-black organic gyttja composed of fine silts and clays but with some macroscopic plant and molluscan shell remains. The macrofossils were mainly present in discrete horizons, the most significant being a layer of weed, possibly the Stoneworts *Chara vulgaris* or *Nitella flexilis*. The plants were not sufficiently well preserved for more exact identification, but cores M1, M2 and M12 contained remains of the lime coating associated with the stems of these algae (Clegg, 1989). Mollusc shells also appeared to be represented in discrete horizons, sometimes in association with a filamentous algae which could not be identified. Molluscan remains are considered in more detail in section 4.4. Core M5 contained very little plant material and few horizons of shells. Pebbles were present in some of the cores at various depths.

A sharp, but not horizontal boundary, separated the upper sediments from a red to reddish brown minerogenic clay beneath. These lower sediments contained few shells or plant remains in comparison with the gyttja above. Of the 12 cores sampled on the grid at Swanswell Pool, 3 did not penetrate deeply enough into the sediment to contain any of the red clay. The average depth of the red clay-gyttja boundary was 42 cm although core M1 reached a depth of 72 cm without encountering the red clay. Core M2, near to the dam wall in the southeast corner of the Pool, penetrated the red clay at 78 cm; the deepest point at which the boundary was encountered. The shallowest the boundary was encountered was

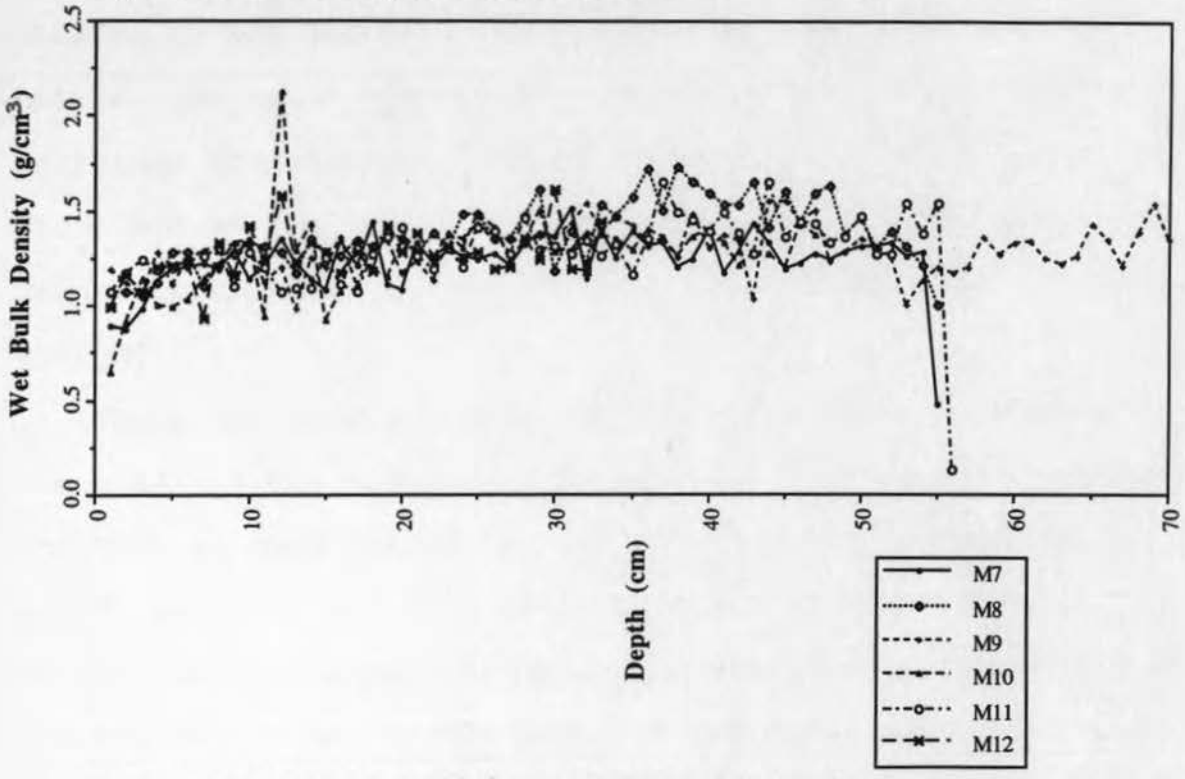
in core M9, located between the western edge of the Pool and the island, where red clay was found at 29 cm.

There are therefore several horizons of both Mollusca and algae present in several of the lake cores. However, none of these are present in all the cores to provide a correlatable horizon across the lake. Similarly, 3 of the cores did not penetrate the red clay, so this was not correlatable across the whole lake using visual stratigraphy alone. From the visual stratigraphy, however, the sediments reveal a twofold sedimentation pattern: an earlier, predominantly minerogenic phase depositing the red clay and a later predominantly organic phase represented by the gyttja. Provisionally this may be interpreted in terms of the red clay being deposited whilst the Springfield Brook was still contributing sediment to the Pool (Chapter 3.4.1) and the transition to deposition of gyttja when the Brook was culverted to the east of the Pool in about 1850.

4.2.3 Bulk density and loss on ignition

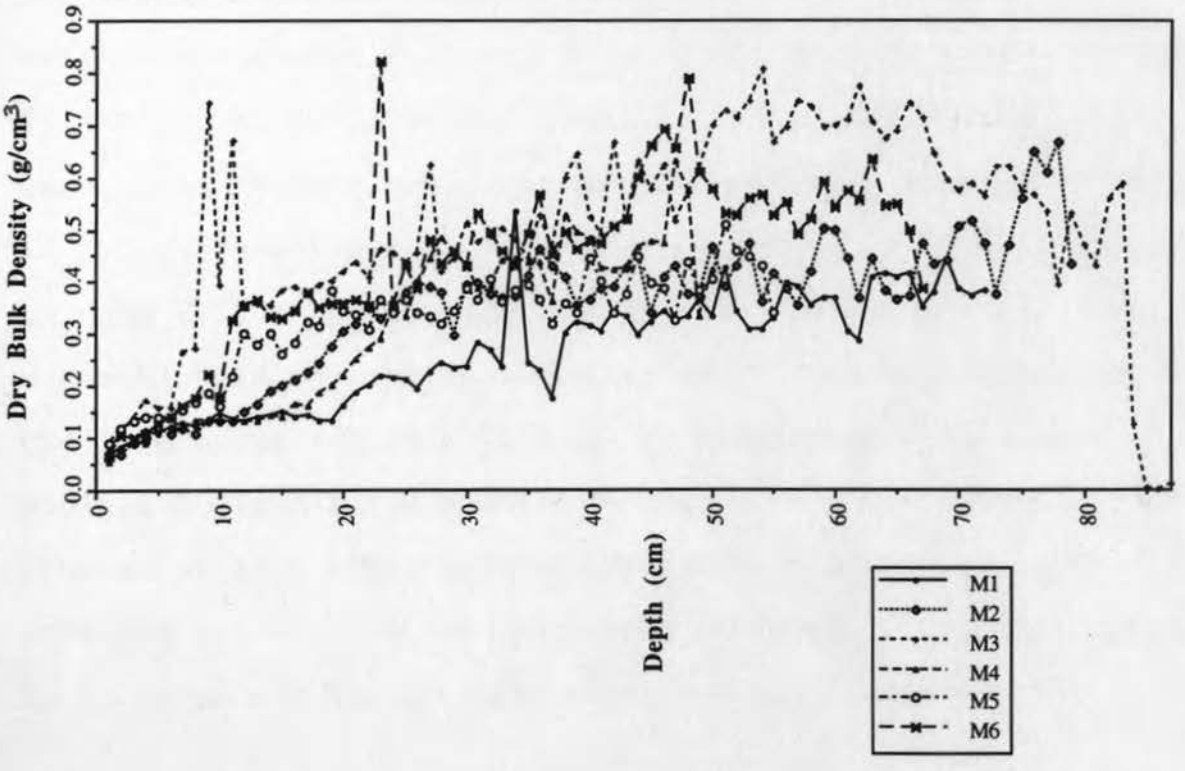
Results obtained for wet and dry bulk density are shown in Figs 4.5 and 4.6. Wet bulk density did not increase markedly downcore at any of the sites, varying from 0.6 to 1.2 g cm^{-3} at the top of the core and from 1 and 1.7 g cm^{-3} at the bottom of the core. The dry bulk density showed some variation between sites, and a gradual increase downcore; particularly at the boundary between the gyttja and the red clay in those cores which extended deep enough. The values ranged from 0.04 to 0.14 g cm^{-3} in the gyttja. The highest value, in core M8,

Fig 4.5 Wet bulk density of cores M7 - M12



Red clay / black gyttja boundary if present
M2 = 78 cm, M3 = 48 cm, M6 = 45 cm, M7 = 48 cm, M8 = 34 cm, M9 = 26 cm, M10 = 47 cm, M11 = 36 cm, M12 = 31 cm

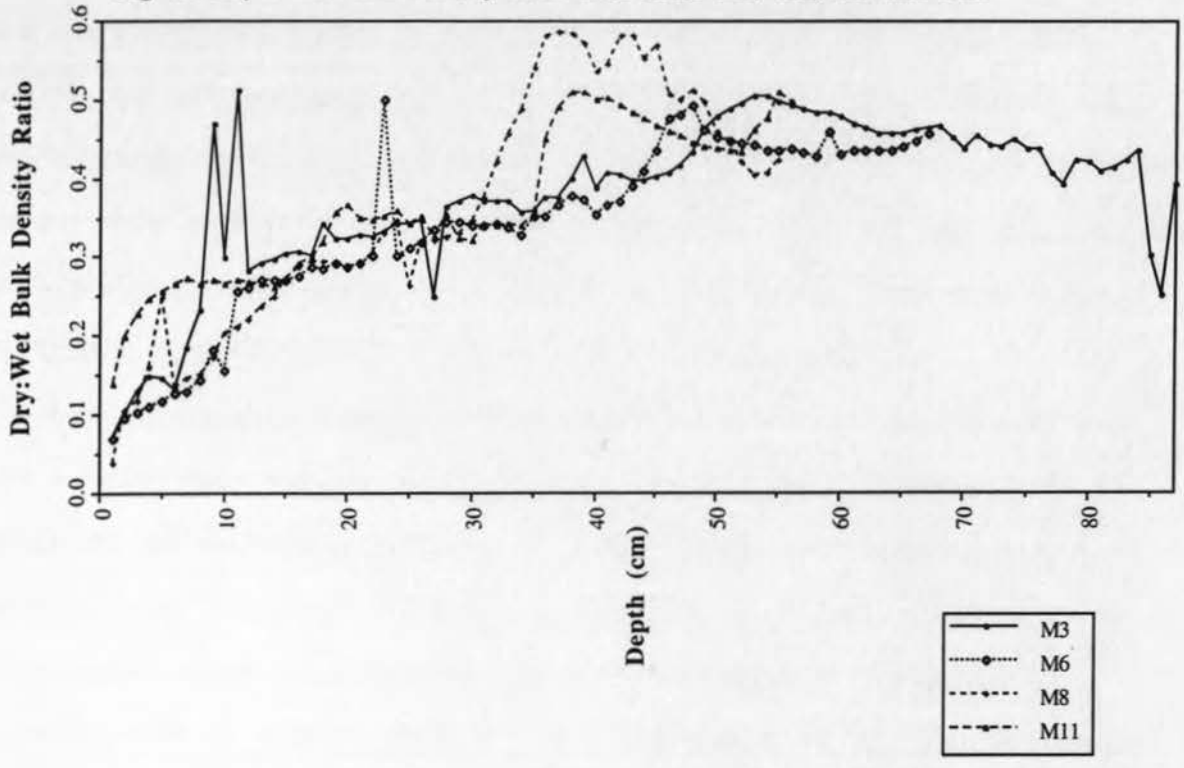
Fig 4.6 Dry bulk density of cores M1 - M6



was 1.18 g cm^{-3}. In the red clay values varied between 0.4 and 1.0 g cm^{-3}. Core M8, from the eastern side of the Pool, had consistently higher dry bulk density values whilst core M1, located in the southeastern corner, had consistently lower values. The ratio between dry and wet bulk densities (Fig 4.7) increases from between 0.04 and 0.14 in the upper samples to about 0.5 at the bottom of the cores, but no significant change is apparent at the boundary between the red clay and gyttja.

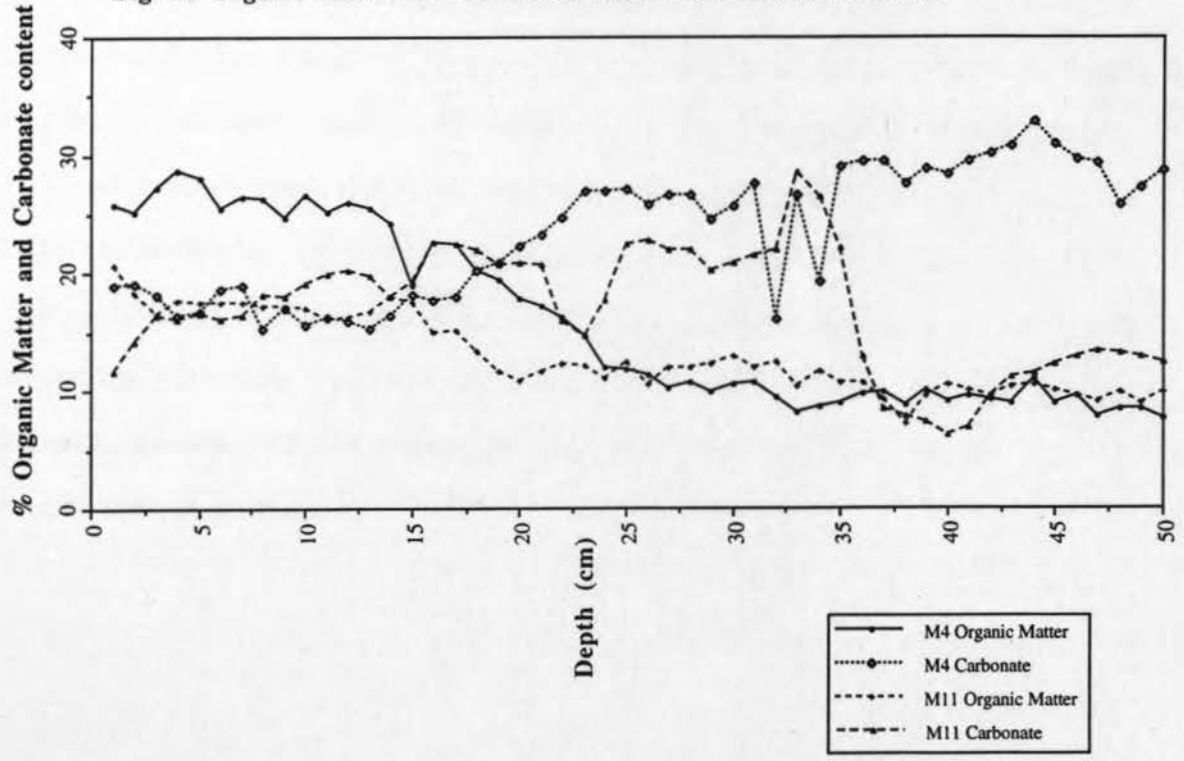
The profiles for organic matter and carbonate content in cores M4 and M11 are shown in Fig 4.8. The general trends are for both of these parameters to decrease with increasing depth, although the carbonate contents are more variable. The organic matter content of core M11, situated in the centre of the transect taken in the north of the pool, declines from a value of 20% to 7% at the boundary with the red clay at a depth of 36 cm. The rise to 10% within the red clay is maintained to the bottom of the core. Values for organic matter are generally higher in core M4, varying from a maximum of 26% in the upper samples down to 10% at the bottom of the core. Core M4 does not penetrate the red clay therefore there is no equivalent decrease in organic matter to that observed in core M11, although there is an isolated decrease to 19% at a depth of 15 cm. Values are over 20% in the upper samples of the lake cores and this is high in comparison with other Midland England lakes such as Merevale Lake and Seeswood Pool (Foster *et al.*, 1987) with organic matter values of 0.75 - 5.9% and 9.2 - 11.6% respectively. Swanswell Pool would appear to be in receipt of high organic matter contributions

Fig 4.7 Dry : Wet bulk density ratio from cores M3, M6, M8 and M11



Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm

Fig 4.8 Organic matter and carbonate content of cores M4 and M11



either from the catchment, or internally due to high productivity. As explained in Chapter 3.4.1, Swanswell Pool has no contributing catchment apart from limited runoff from the surrounding park. Chapter 3.3.1 detailed the waterfowl living on and around the Pool. It therefore seems likely that the organic matter reflects high internal productivity at this site. This could be due to the water fowl living on and around the Pool, (see Chapter 3.3.1) which are known to cause high sediment organic matter (Gere & Androvics, 1992).

The carbonate content in core M11, whilst decreasing from 33% in the top sample to 22.5% at the bottom, initially exhibits an increase downcore. This trend is interrupted by a marked drop to 26.5% between 17 and 25 cm depth. The subsequent rise in carbonate content downcore is again interrupted at the boundary with the red clay where carbonate content decreases to 15% before rising again to the bottom of the core. The carbonate content is generally higher in core M4 than in core M11. Initially exceeding 61%, it falls to 34% at 33cm depth. The deepest sample at 50cm reaches a value of 62%, but those between 36cm and 49cm, whilst fluctuating slightly, still decrease towards the basal sediments. Unlike in sea water, carbonate is not entirely removed by biota (Stumm & Morgan, 1981), although comparison of the stratigraphies (Fig 4.4) with Fig 4.8 indicates increased carbonate content of the sediment where shells remains and the carbonate-rich Stoneworts appear.

4.2.4 Sediment Chemistry

The results of sediment chemical analysis are presented in the following section which is divided into three parts. With the aim of reconstructing pollution history in the lake, downcore trends of metal concentration are presented first followed by analysis of the spatial distribution of metals in the upper 1 cm of lake sediment in the 12 cores taken in the grid shown on Fig 2.7a.

As discussed in Chapter 2.11, P, Fe and Mn are used in this study as indicators of past nutrient and redox status, and their distribution is also considered both downcore and spatially.

The third section is concerned with the non-metallic elements. These can indicate past sedimentation regimes, such as increased erosion (Engstrom & Wright, 1984) which may help to identify changing sediment sources or changing sediment yield. Non-metallic elements may also indicate changing salt concentrations over time which could lead to the release of heavy metals into the water column (Chapter 2.8 v).

1. Heavy metal analysis

a. Trends in heavy metal concentration with depth.

This section is divided into two parts, with a consideration of the analysis for the total heavy metal concentration downcore presented first followed by a discussion of the

results of a sequential extraction carried out on one lake core.

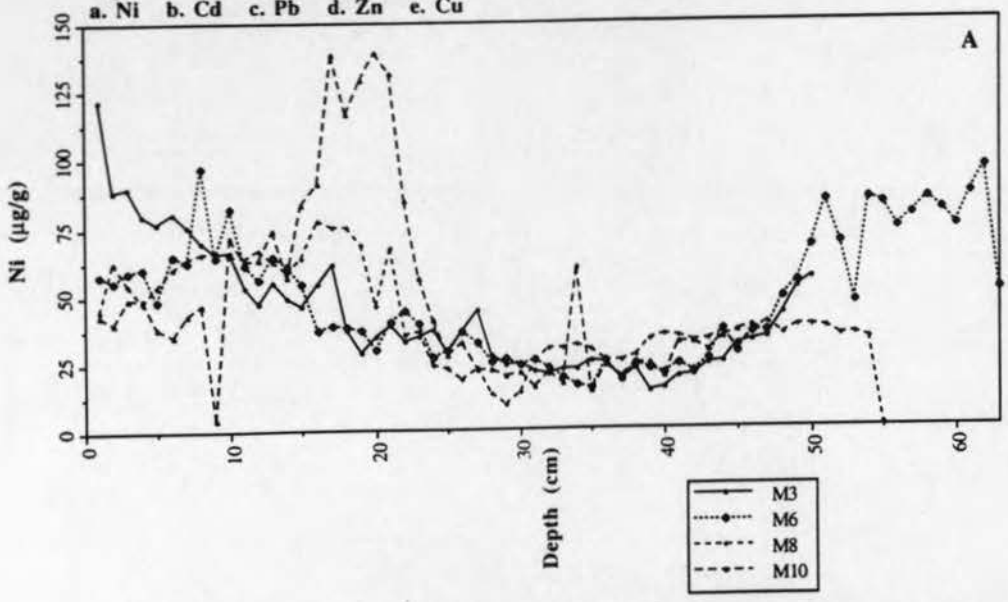
i. Total extraction of heavy metals

The general trend in the lake cores is for a decrease in the concentration of heavy metals with depth; the exception being Ni (Fig 4.9 a) which exhibits an increase in the basal sediments below the interface between the organic gyttja and the red clay. Ni concentrations range from a maximum of 140 $\mu g\ g^{-1}$ at a depth of 20 cm in core M10 to a minimum of 4 $\mu g\ g^{-1}$ at a depth of 9 cm, also in core M10. The decrease in Ni concentration in the top few cm is followed by a substantial rise; the largest being found in core M10, and the smallest peak in core M3. Concentrations then decrease to the boundary with the red clay whereupon they increase again.

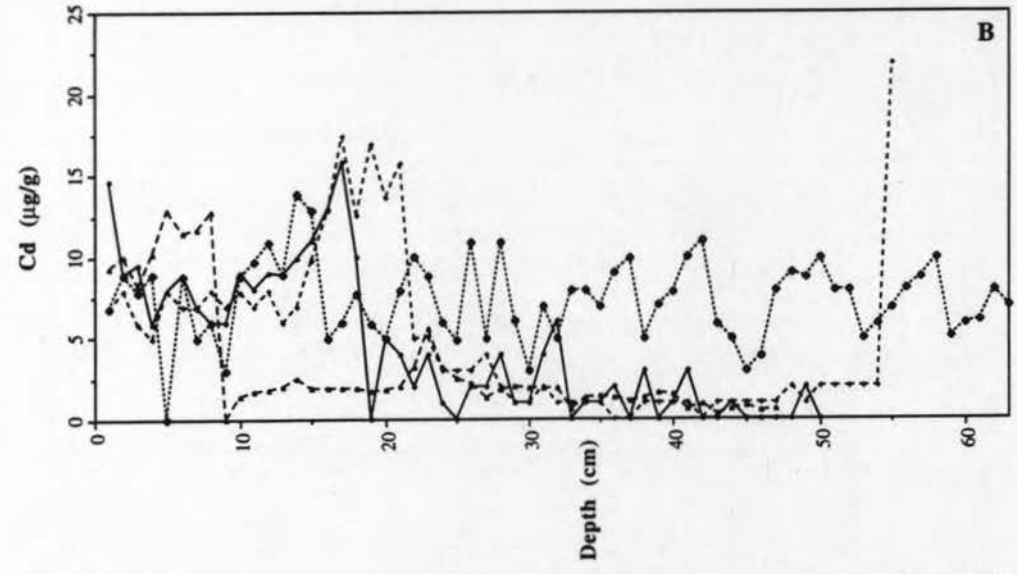
The profile for Cd (Fig 4.9b) fluctuates between the limits of detection and 18 $\mu g\ g^{-1}$ with generally the lowest concentrations found in core M10 and the highest in core M8. In general, concentrations are higher in the upper sediments of the core, although average values in core M6 do not decrease below 20 cm depth.

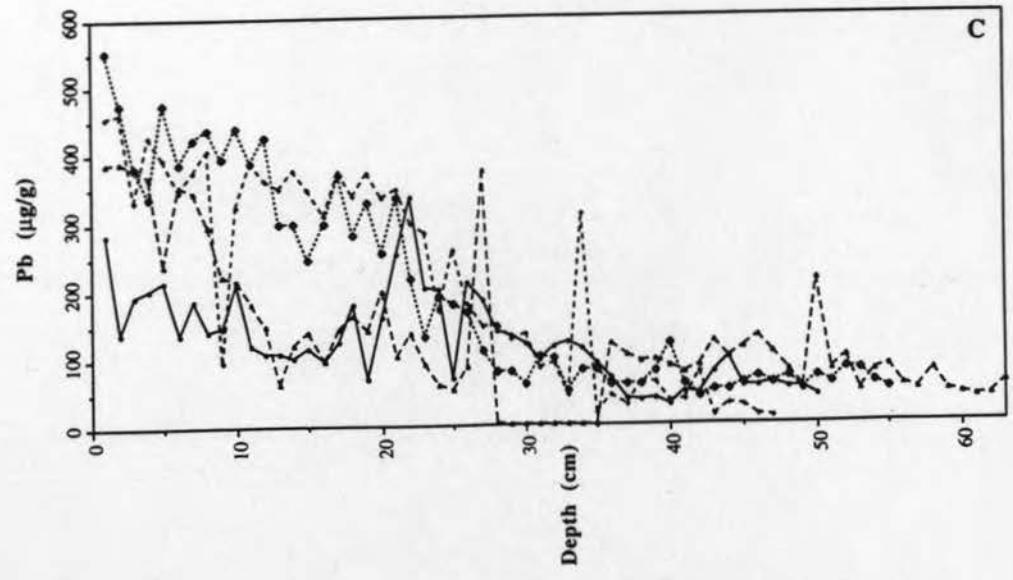
Pb concentrations (Fig 4.9c) show great variability in all cores, although the underlying trend is for this metal to decrease in concentration with depth. Values vary from a maximum of 550 $\mu g\ g^{-1}$ recorded from the top sample of core M8 down to between 29 and 35 cm depth in core M6 where Pb concentration is below the limit of detection.

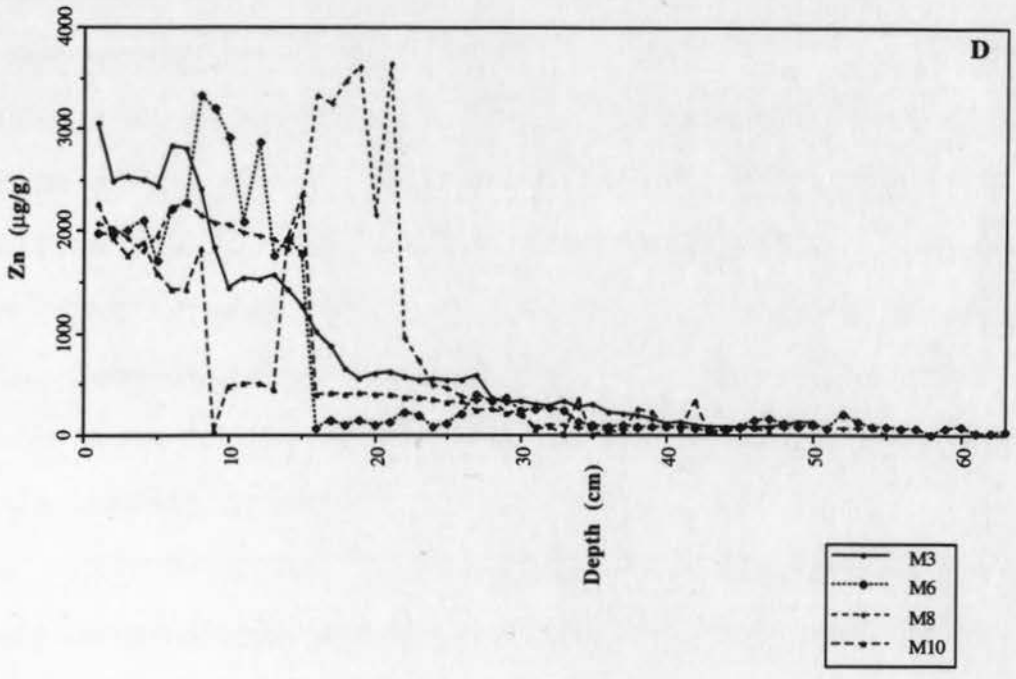
Fig 4.9 Total heavy metal content of lake sediment cores
a. Ni b. Cd c. Pb d. Zn e. Cu



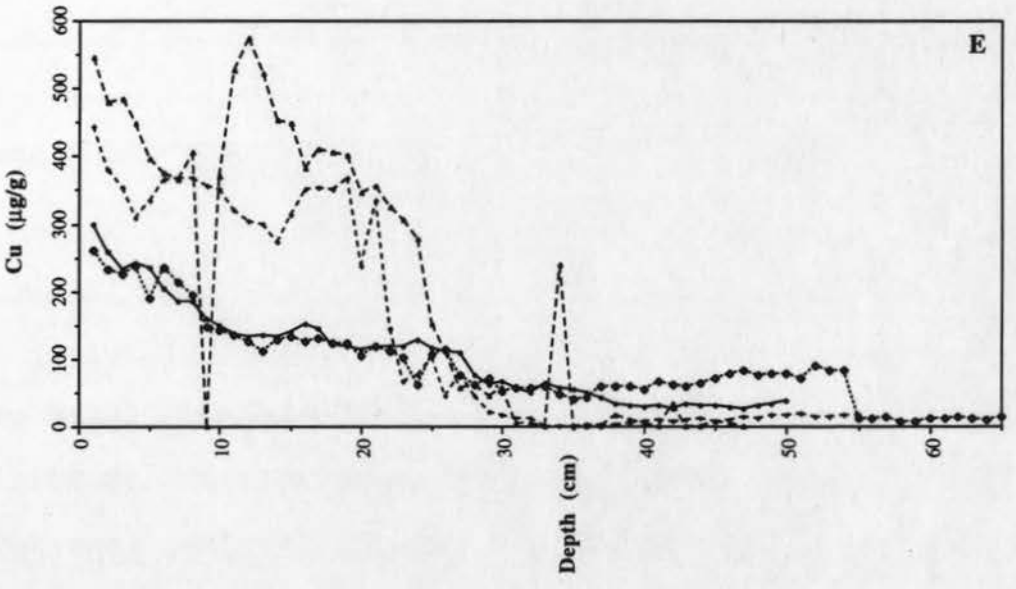
Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm







Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm



Zn concentration decreases in the top few cm of all cores, exhibits a slight increase and then decreases, until by 30 cm depth it is mostly undetectable. The increase in core M8 is found lower than the other cores at 15 cm and reaches a maximum concentration of 3700 $\mu g\ g^{-1}$.

Cu (Fig 4.10 e) exhibits a fall in concentration in the upper 30 cm of all cores. In core M10, Cu is undetectable at 9 cm, immediately before the highest concentration of 57 $\mu g\ g^{-1}$ at 10 cm depth is recorded. The sample at 9 cm depth in core 10 has low concentrations for all the heavy metals analysed, whereas at 34 cm in the same core there is a marked peak in all metals concentrations.

Table 4.1 summarises the maximum total concentrations of heavy metals recovered in the Swanswell Pool lake sediments.

Table 4.1 Maximum concentrations of heavy metals from the Swanswell Pool lake sediments ($\mu g\ g^{-1}$).

Zn	Ni	Cu	Pb	Cd
3700	140	600	550	18

The heavy metal chemistry is dominated by Zn, followed by Cu and Pb, with Ni and particularly Cd present in lower concentrations. However, Chapter 2.4, Table 2.4, shows that Cd

is not an essential element and would be toxic to biota even in small amounts (Macklin, 1992 and Table 2.6).

The trend of heavy metal accumulation over time in Swanswell Pool is of increasing concentration from just above the red clay / gyttja boundary to the present day. In order to assess the magnitude of this increase, background values from uncontaminated deposits should be compared with the values obtained from Swanswell Pool. Section 4.2.2 suggests that the gyttja / red clay boundary may represent the time when the Springfield Brook was cut off from the Swanswell Pool. The relatively low and constant heavy metal concentrations in the red clay tend to support this assumption. If it is the case that the boundary between the two sediment types represents 1850, then the red clay could provide samples of sediment laid down before the Industrial Revolution and therefore before the onset of contamination by anthropogenic heavy metal release. Comparison of average heavy metal concentrations from the red clay and published background values (Förstner & Salomons, 1981a) would also provide confirmation of their pre-Industrial Revolution origins. Table 4.2 presents a comparison between background concentrations and average concentrations of heavy metals in the red clay at Swanswell Pool. This shows that Zn, Ni, and Cu are all comparable with the published data, but Pb and Cd are slightly higher, which may reflect the local geology rather than any enrichment due to cultural effects. The red clay was therefore used as a background value in any calculations of anthropogenic excess heavy metal delivery to Swanswell Pool.

Table 4.2 Comparison between heavy metal concentrations in published background values of sediments and average values for the red clay from Swanswell Pool ($\mu g\ g^{-1}$).

	1	2	3	4	5
Zn	105	115	118	95	65
Ni	51	46	66	68	55
Cu	25	51	45	45	30
Pb	16	30	34	20	50
Cd	0.2	0.3	0.4	0.3	0.8

1. Fossil lake sediments (Ries Lake n=25)
2. Fossil river sediments (Rhine n=4)
3. Recent lake sediments from remote areas (n=87)
4. Shale standard

Source: Förstner & Salomons (1981a)

5. Red minerogenic clay at the base of Swanswell Pool (n=63)

From background values and maximum concentrations of heavy metals obtained from the lake cores, enrichment factors can be calculated. This is a measure of cultural enhancement of heavy metal content (Förstner & Wittmann, 1981), where the enrichment factor (F) is defined as:

$$F = \frac{\text{maximum value}^*}{\text{background value}^{**}}$$

* taken from concentrations given in Table 4.1

** taken from concentrations given in Table 4.2, column 5

Table 4.3 gives values of F for the lake sediments from Swanswell Pool. All metals are significantly enriched, in particular Zn and Cd. To put these values into perspective, they are compared with those for Wyken Pool in Table 5.4 in Chapter 5.2.4 and also with other published values of F from lakes in the USA.

Table 4.3 Cultural enrichment factors (F) for Swanswell Pool lake sediments

	Zn	Ni	Cu	Pb	Cd
F	55.4	2.6	20.0	11.0	22.5

ii. Sequential extraction of heavy metals

This section is discussed under two separate headings to discriminate between the partitioning of heavy metals in the sediments and also the overall trend of metal concentrations with depth in the sediment column.

1. Partitioning of heavy metals in the sediments of Swanswell Pool

Table 4.4 lists the primary and secondary sinks within the sediments for the individual metals. Fe and Mn oxides dominate for Pb, Ni and Zn, probably in the form of cements or coatings on grains (Tessier *et al.*, 1979) whilst a secondary sink for Pb and Ni is organic matter. Zn and Cu are found predominantly in the exchangeable fraction, whilst carbonates are the only other form in which Cu is detectable. With the exception of the residual minerals in which the concentration of Cd remains at minimal levels throughout, there is no fraction which can be said to dominate the retention of Cd. There is no evidence to suggest any fundamental change in partitioning of the heavy metals through time in Swanswell Pool. Release of heavy metals from Fe and Mn cements and organic matter would only occur with changing redox conditions (Chapter 2.4 iib), exchangeable sites would provide the most concern since Zn or Cu could be released in acidic conditions (Chapter 2.4 iib). Chapter 3.4.1 highlighted the periodic spillages that have occurred in Swanswell Pool in the past. Section 4.5 discusses water quality in Swanswell Pool and this will be applied back to the partitioning of heavy metals in sediments described in this section.

Table 4.4 Fractions associated with the highest proportion of metals in the upper zone.

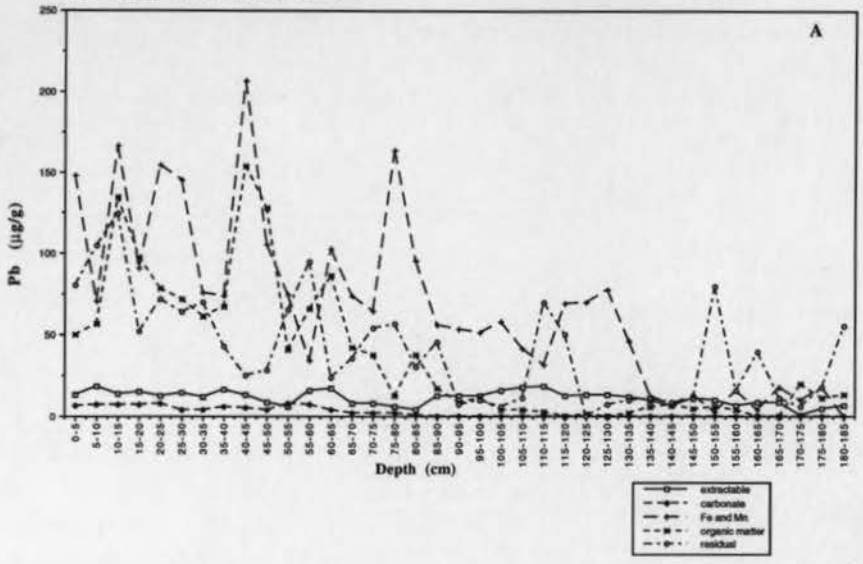
element	fractions
Pb	Fe and Mn; organic matter
Ni	Fe and Mn; organic matter
Zn	Fe and Mn; exchangeable
Cd	none dominates
Cu	exchangeable; carbonate

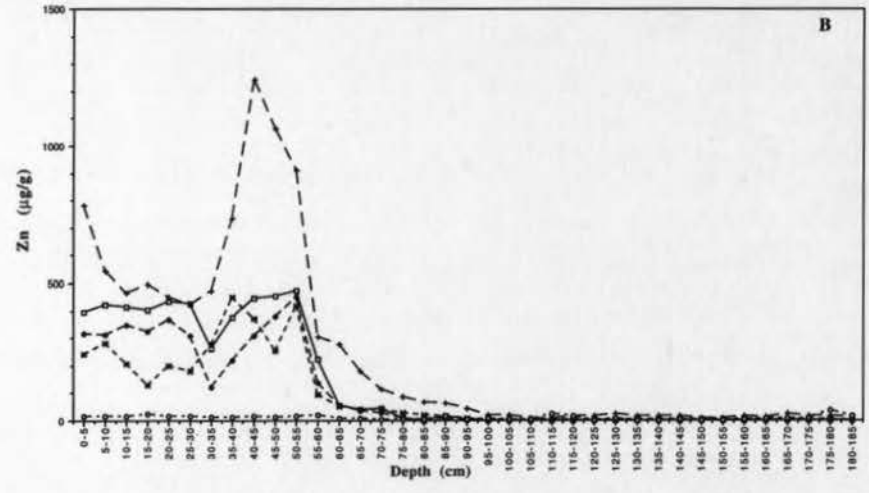
2. Trends of metal concentration with depth in the sediment of Swanswell Pool

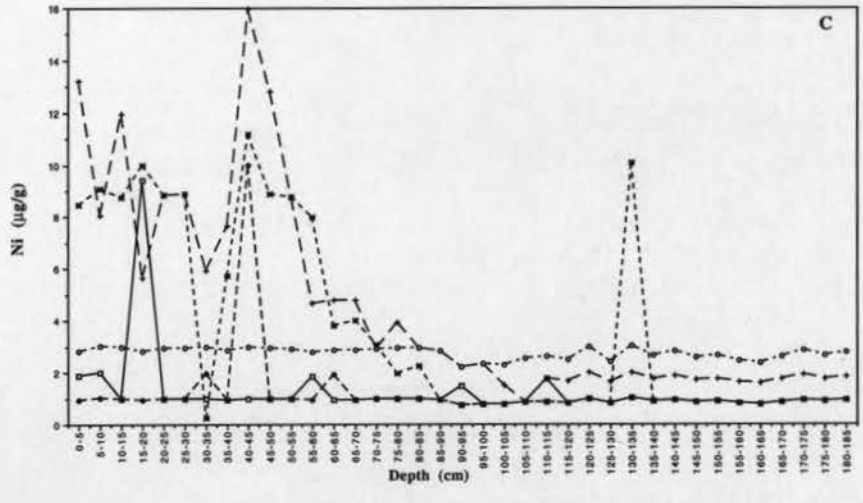
The fractionation of the lake sediments in core P2 (Fig 2.7 a) yielded profiles which can be divided into two broad zones. In the upper zone, down to about 70cm (the red clay was encountered at 90 cm), concentrations of the metals are generally higher than in the sediments below (Figs 4.10 a - e). There are, however, fractions in which the concentration of all metals vary little, if any, downcore. These are identified in Table 4.5.

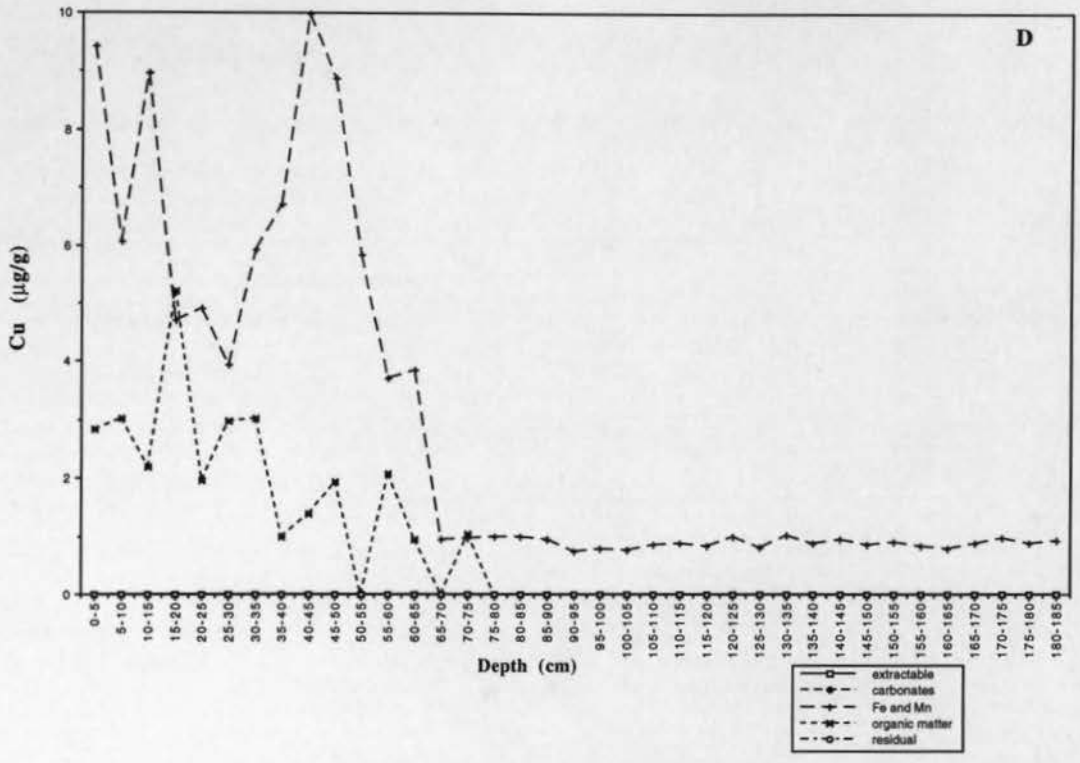
Pb (Fig 4.10 a) is as variable in the fractionation profile as in the total digest, although the concentration of Pb in the red clay is lower than that in the sediments above. The Zn and Ni (Fig 4.10 b and c) profiles are marked by peaks

Fig 4.10 Sequential heavy metal extraction of lake sediment cores
a. Pb b. Zn c. Ni d. Cu e. Cd








D
Cu (µg/g)
Depth (cm)
extractable
carbonates
Fe and Mn
organic matter
residual

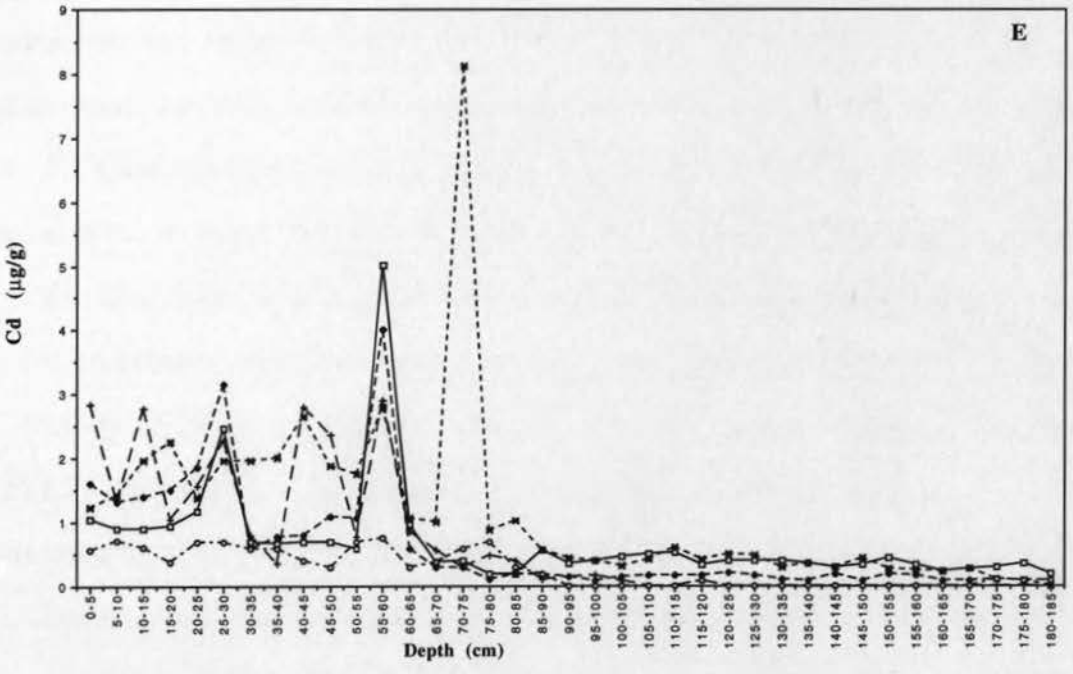

E
Cd (µg/g)
Depth (cm)

Table 4.5 Fractions with no variation downcore.

element	Fraction
Pb	exchangeable; carbonate
Ni	residual; carbonate
Zn	residual
Cd	residual
Cu	residual; Fe and Mn; organic matter

in concentration between samples 7 and 13 in which they are particularly enriched in association with Fe and Mn oxides. Subsequently, concentrations in all the fractions fall to background levels with increasing depth. There is an isolated peak in the concentration of Ni bound to organic matter in sample 27. A peak in Cd concentration occurs in sample 12 in all but the residual minerals (Fig 4.10 d). A single peak in the Cd content of the organic matter fraction occurs in sample 15. The peak for Cu (Fig 4.10 e) in the upper sediments is slightly broader, encompassing samples 6 to 14 in the exchangeable fraction. The trend in Cu bound to carbonates is for decreasing concentrations with increasing depth, apart from a peak in sample 4. Below sample 14, Cu is only detectable in the exchangeable fraction.

Sample 9, at a depth of 45 cm, marks a peak in the concentration of all the elements, although not necessarily in all of the fractions.

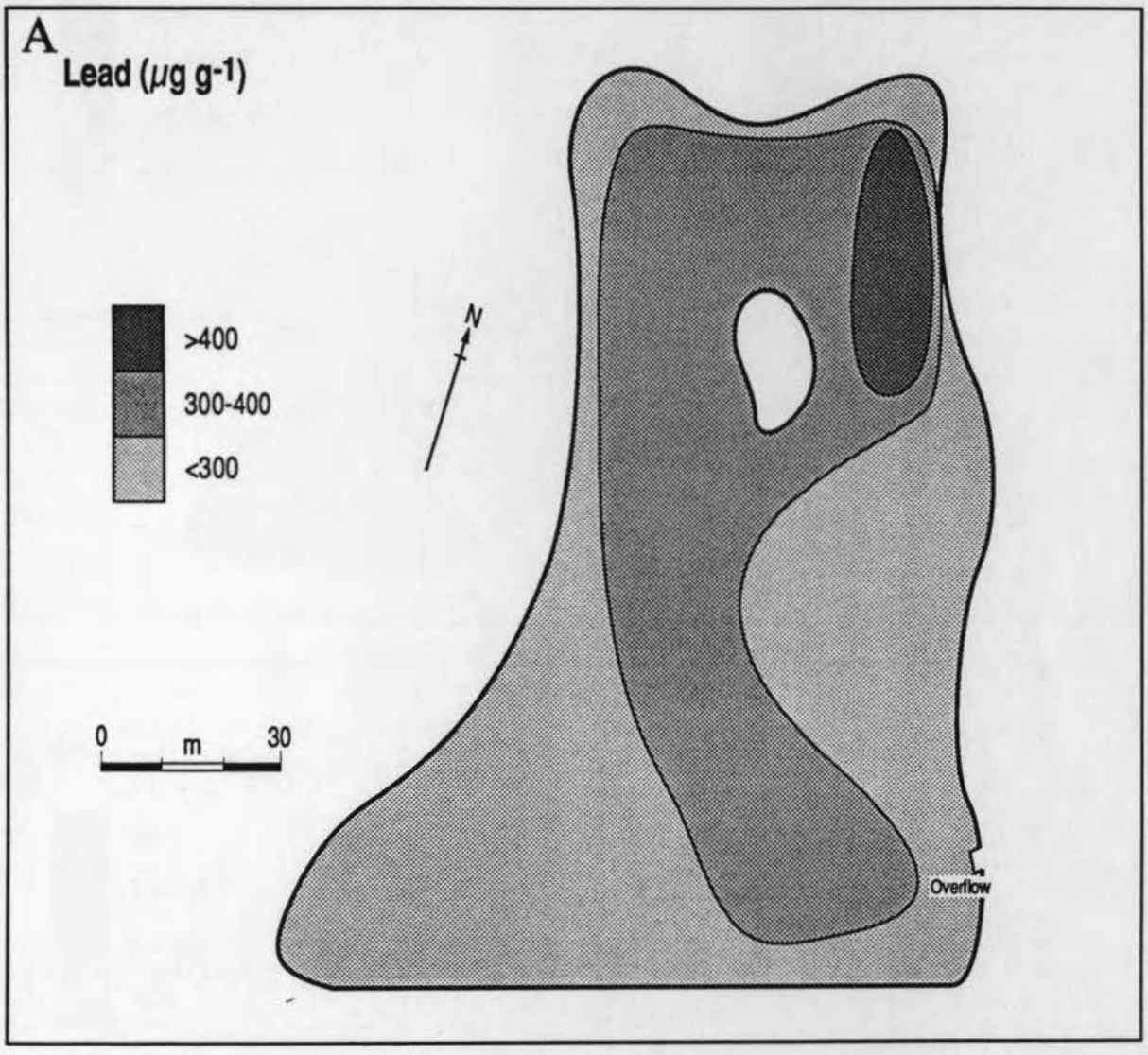
The overall trends in the sequential extractions reflect those found in the total extraction; that of increasing metal concentration towards the present day and with low, constant values from just above the gyttja / red clay boundary to the base of the core.

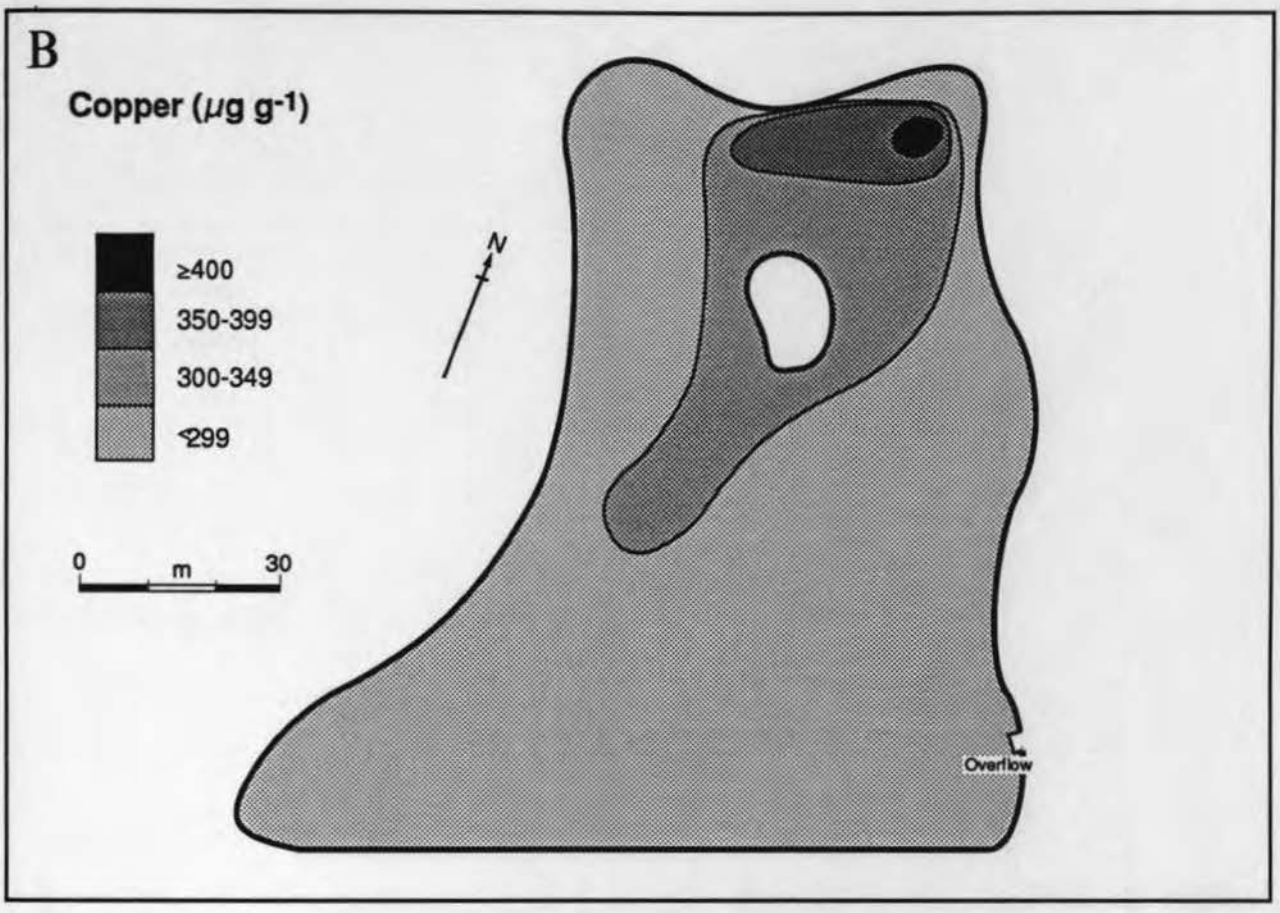
b. The spatial distribution of heavy metals in the top 1 cm sediments of the Pool.

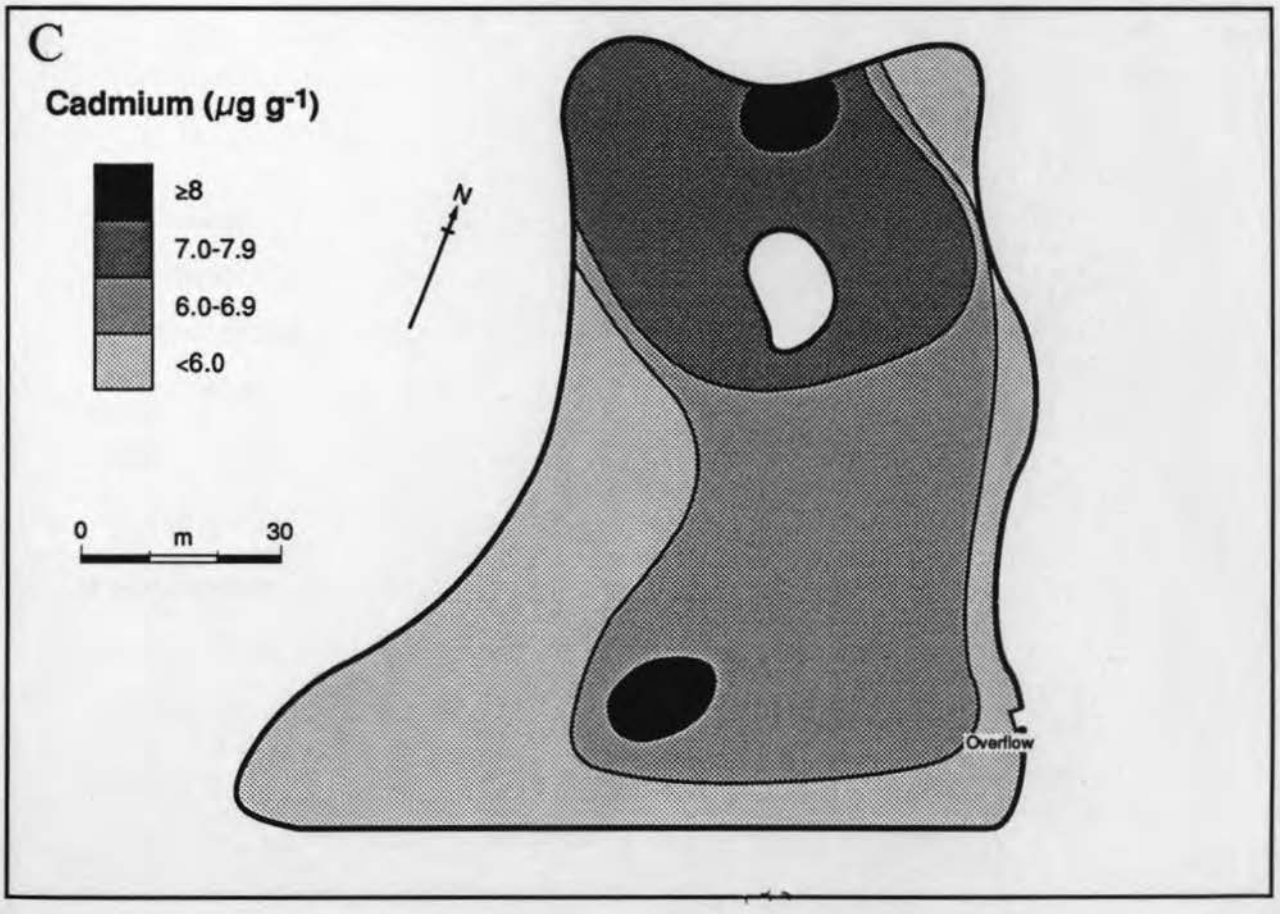
The results of heavy metal analysis of the upper 1 cm samples from each of the cores in the grid at Swanswell Pool are presented in Figs 4.11 a-e. The pattern for all of the heavy metals is similar, except for Pb. There are two areas of the Pool in which the concentrations of Cd, Cu, Ni and Zn are highest. These are in the north of the Pool, near the hospital settling tank inflow, and in the southern end of the lake at some distance away from the outflow weir. In the case of Pb (Fig 4.11 a), the areas of highest concentration are towards the eastern margins of the Pool, one in the north, to the east of the hospital settling tank, and the second in the south east, near the dam wall. With the exception of Cu and Pb, the concentrations of heavy metals near the outlet are higher than those near the hospital settling tank inflow.

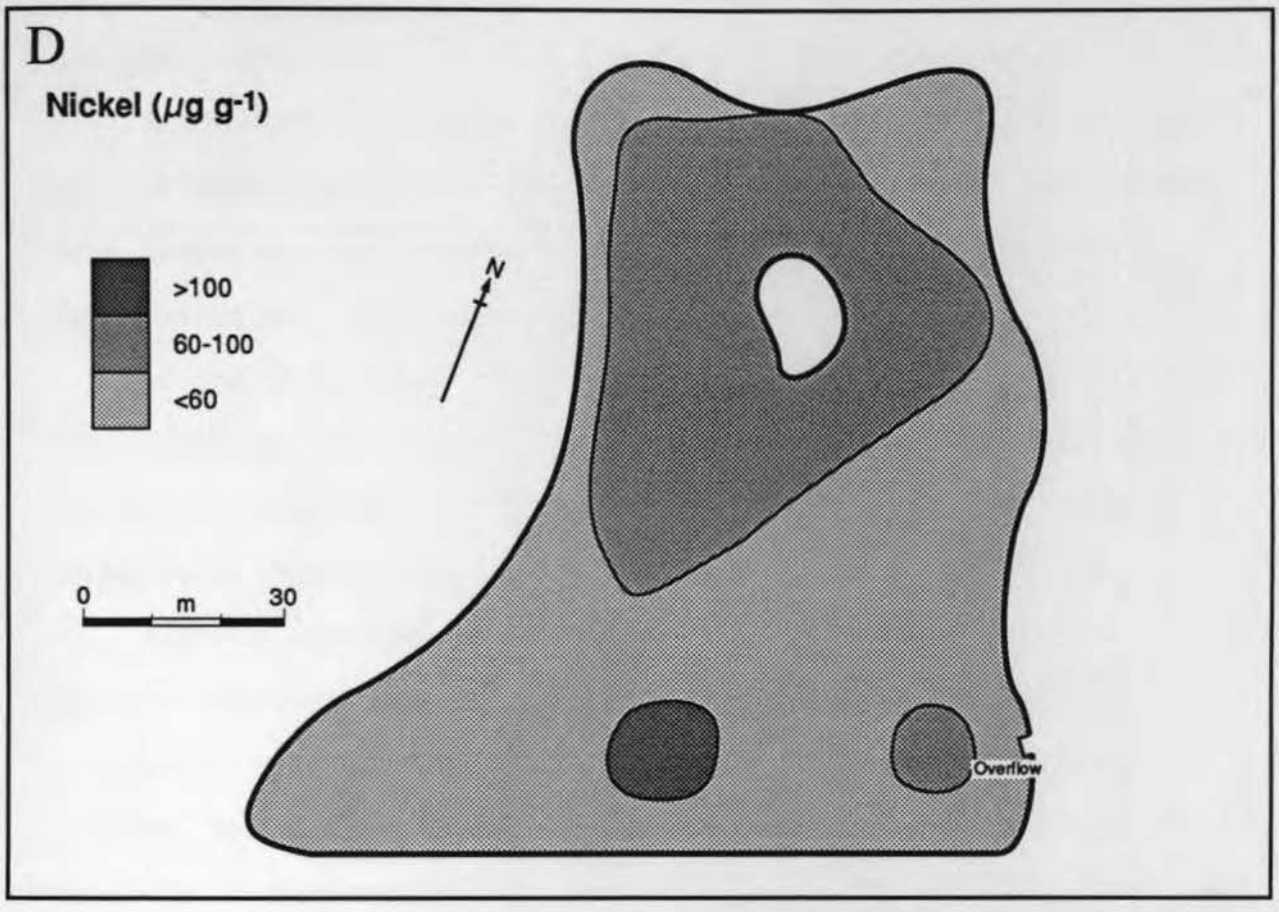
Higher Pb values are found around the northeastern and southeastern margins of the pool, with the minimum value interposed between the two areas of maximum concentration.

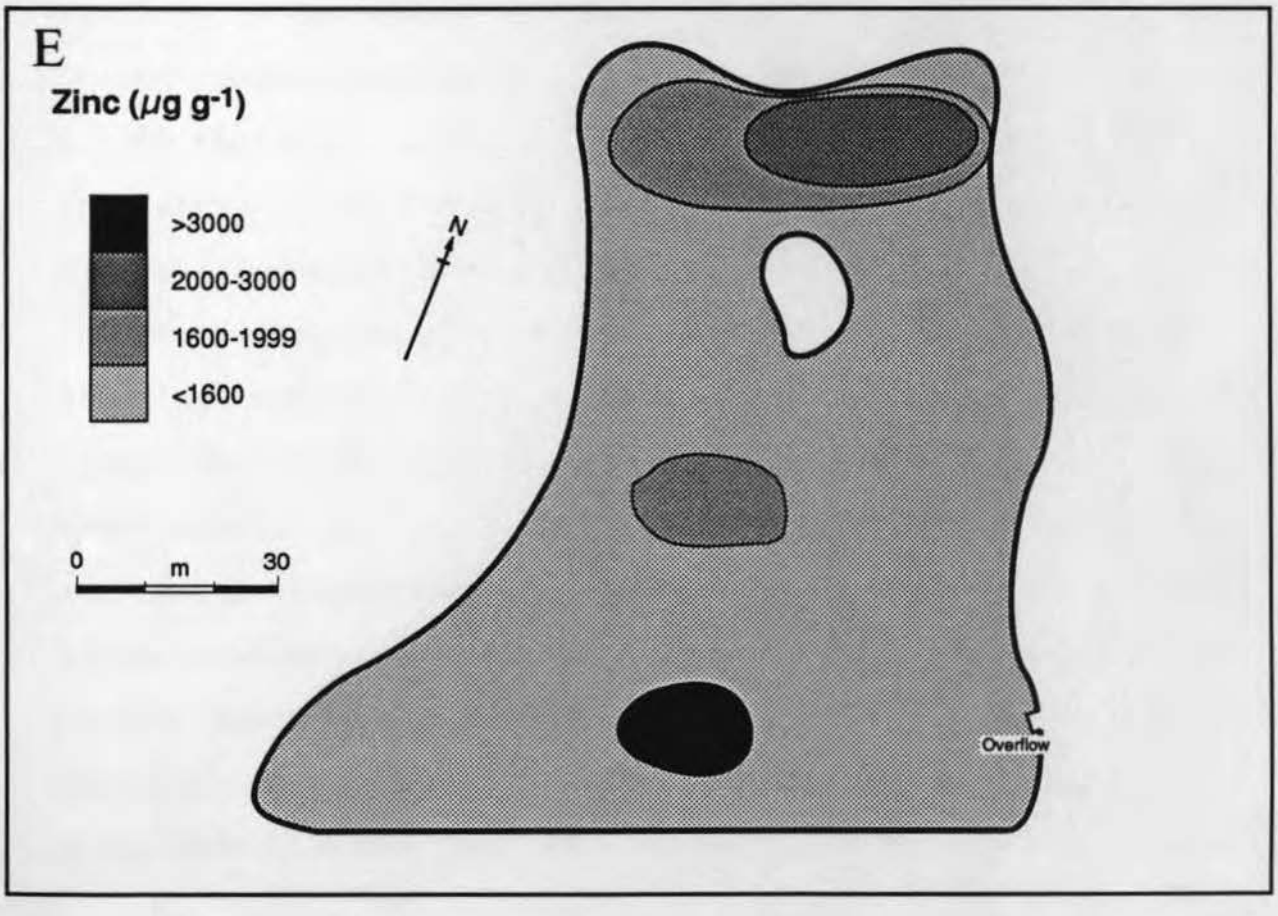
Fig 4.11 Spatial distribution of heavy metals in surface lake sediments :
a. Pb
b. Cu
c. Cd
d. Ni
e. Zn




B
Copper (μg g-1)
≥400
350-399
300-349
<299
N
0
m
30
Overflow


C
Cadmium (μg g-1)
≥8
7.0-7.9
6.0-6.9
<6.0
N
0
m
30
Overflow


D
Nickel (μg g-1)
>100
60-100
<60
N
0
m
30
Overflow


E
Zinc (μg g-1)
>3000
2000-3000
1600-1999
<1600
N
0
m
30
Overflow

Concentrations of Pb tend to decrease towards the central eastern areas of the pool. Values vary from 474 to 233 $\mu g\ g^{-1}$.

Concentrations of Cu (Fig 4.11 b) vary from 54.44 $\mu g\ g^{-1}$ in the northeast corner to 24.8 $\mu g\ g^{-1}$ in the southeast near the overflow. Values tend to decrease in the central and eastern areas, but the range of values is relatively small.

Cd concentrations (Fig 4.11 c) vary from 14.65 $\mu g\ g^{-1}$ in the south to less than 4 $\mu g\ g^{-1}$ in the northeastern corner. Concentrations tend to decrease southwards and towards the margins of the pool.

Maximum concentrations of Ni (Fig 4.11 d) are to be found in the south of the pool at over 120 $\mu g\ g^{-1}$. The minimum concentration of 42.6 $\mu g\ g^{-1}$ is found in the northeastern corner. Apart from these two extremes, values do not vary greatly across the rest of the surface sediments, although the tendency is for concentrations to decrease southwards.

Zn concentrations (Fig 4.11 e) vary between about 3000 $\mu g\ g^{-1}$ in the south, and 1510 $\mu g\ g^{-1}$ in the area to the east of the island. Values tend to decrease around the margins of the pool and towards the overflow.

The historical problems with spillages from the hospital settling tank overflow outlined in Chapter 3 may still be reflected in the sediments with higher concentrations of most heavy metals found in the north of the Pool. Sediment focusing may also be responsible in part for the distribution of metals in the surface sediments, reflecting differential settling of coarser particles near the hospital overflow and finer particles near the Pool overflow accounting for an area of high values there.

2. P, Fe and Mn content of lake sediments

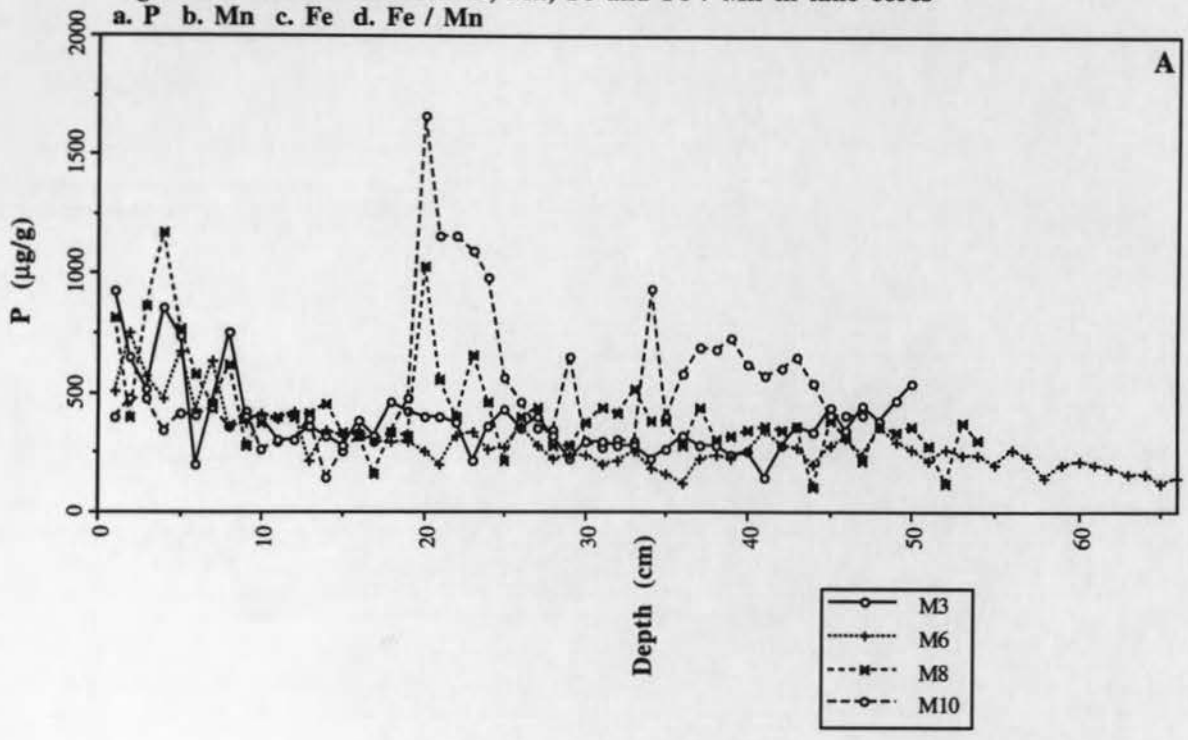
This section is divided into two parts to present the results of the distribution of P, Fe and Mn with depth in the lake sediments and also spatially in the surface samples of the lake.

a. Downcore trends in P, Fe and Mn content

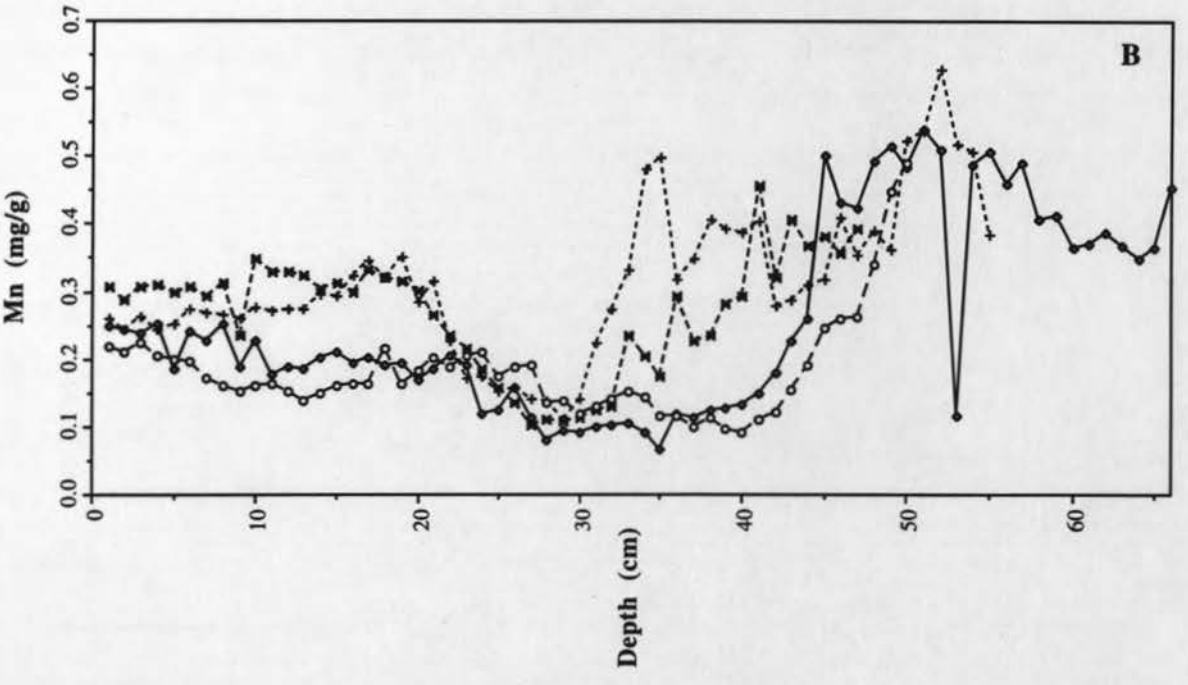
The general trend in P concentration downcore (Fig 4.12 a) is for a perceptible decrease with depth. Concentrations vary from between 200 and 1200 $\mu g\ g^{-1}$ in the upper sediments to between 180 and 400 $\mu g\ g^{-1}$ towards the bottom of the core (cores M6, M8 and M10). Core M3 has a minimum concentration of 200 $\mu g\ g^{-1}$ at 47 cm depth and a maximum of 600 $\mu g\ g^{-1}$ at 53 cm, the base of the core. All cores except core M10, in which concentrations gradually decline, exhibit an increase in concentration in the upper 9 cm. Core M8, for example, approaches 1200 $\mu g\ g^{-1}$ at a depth of 4 cm. The peak in core M10 occurs at a depth of 21 cm where values reach 1660 $\mu g\ g^{-1}$. Secondary peaks are also evident in core M8 at 21 and 23 cm, rising to 1020 and 620 $\mu g\ g^{-1}$ respectively. Whilst P in cores M3, M6 and M8 subsequently decreases in concentration with depth, core M10 exhibits isolated peaks at 29 and 34 cm and a sustained rise from 35 to 45 cm reaching a maximum of 780 $\mu g\ g^{-1}$.

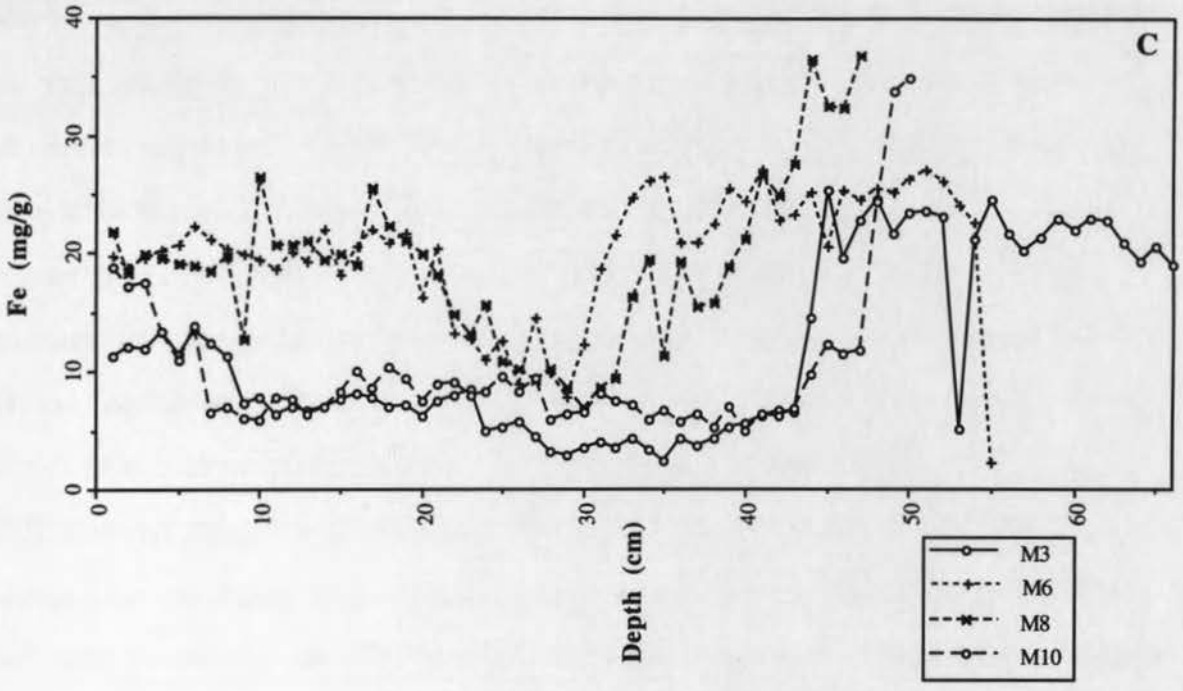
P concentrations do not indicate excessive productivity and hence it is unlikely that Swanswell Pool has suffered problems associated with eutrophication in the past.

Fig 4.12 Downcore trends in P, Mn, Fe and Fe / Mn in lake cores
a. P b. Mn c. Fe d. Fe / Mn

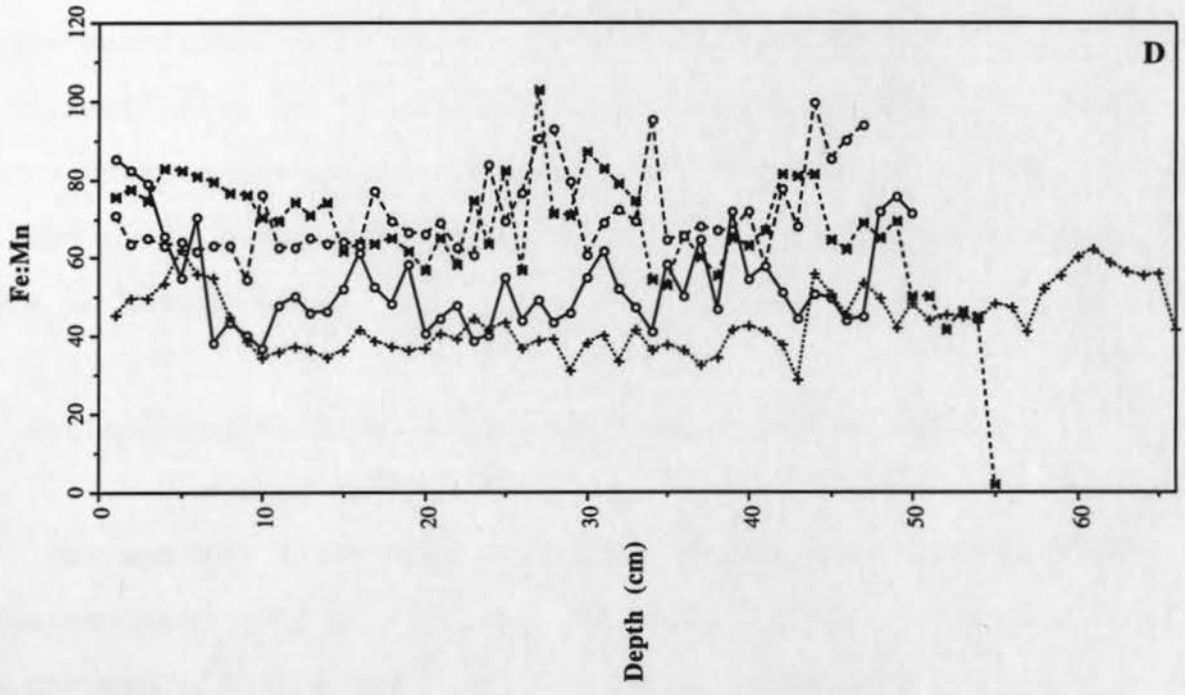


Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm





Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm



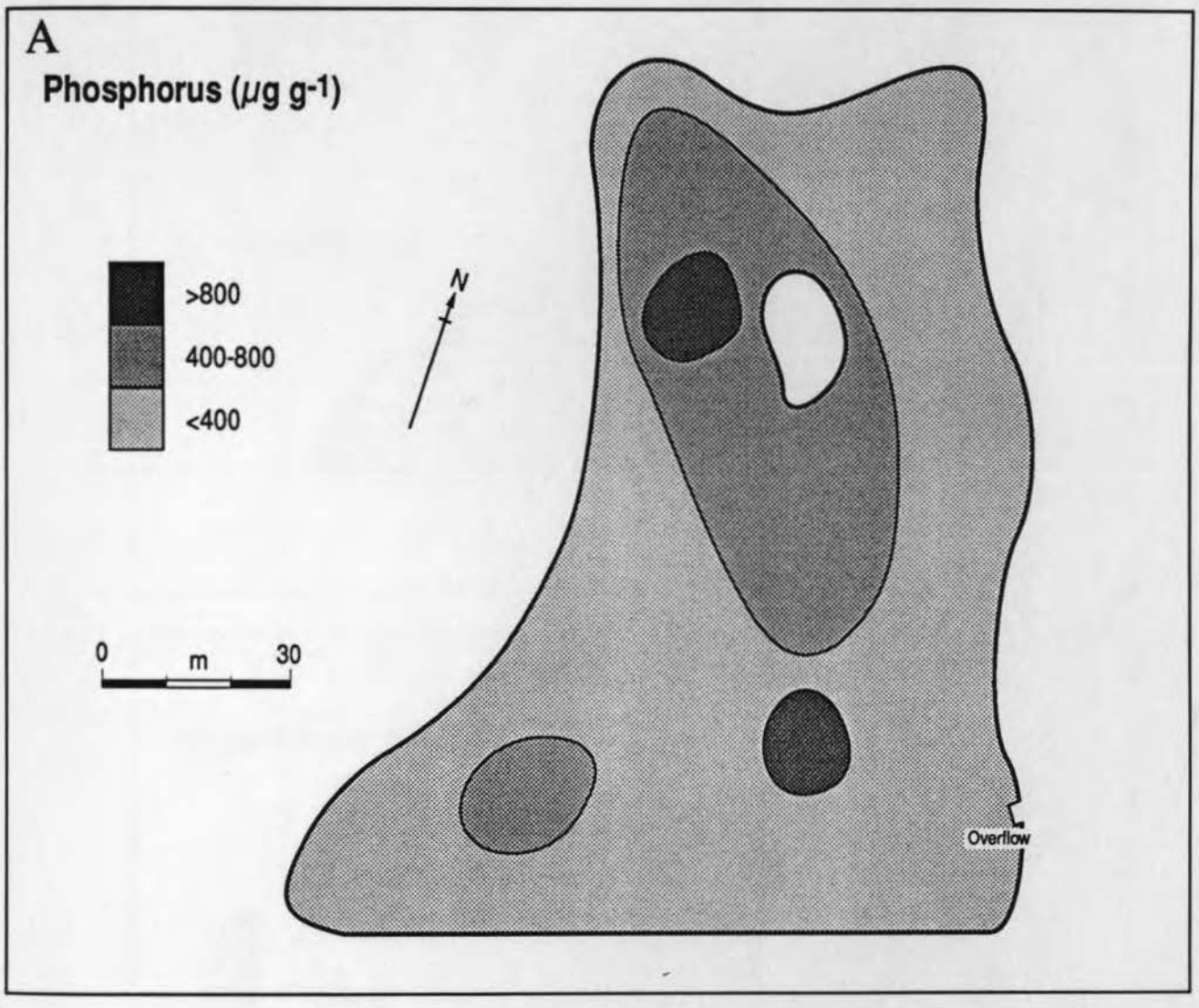
The high organic matter values obtained for the upper lake sediment may be due to the lack of channelled inflow.

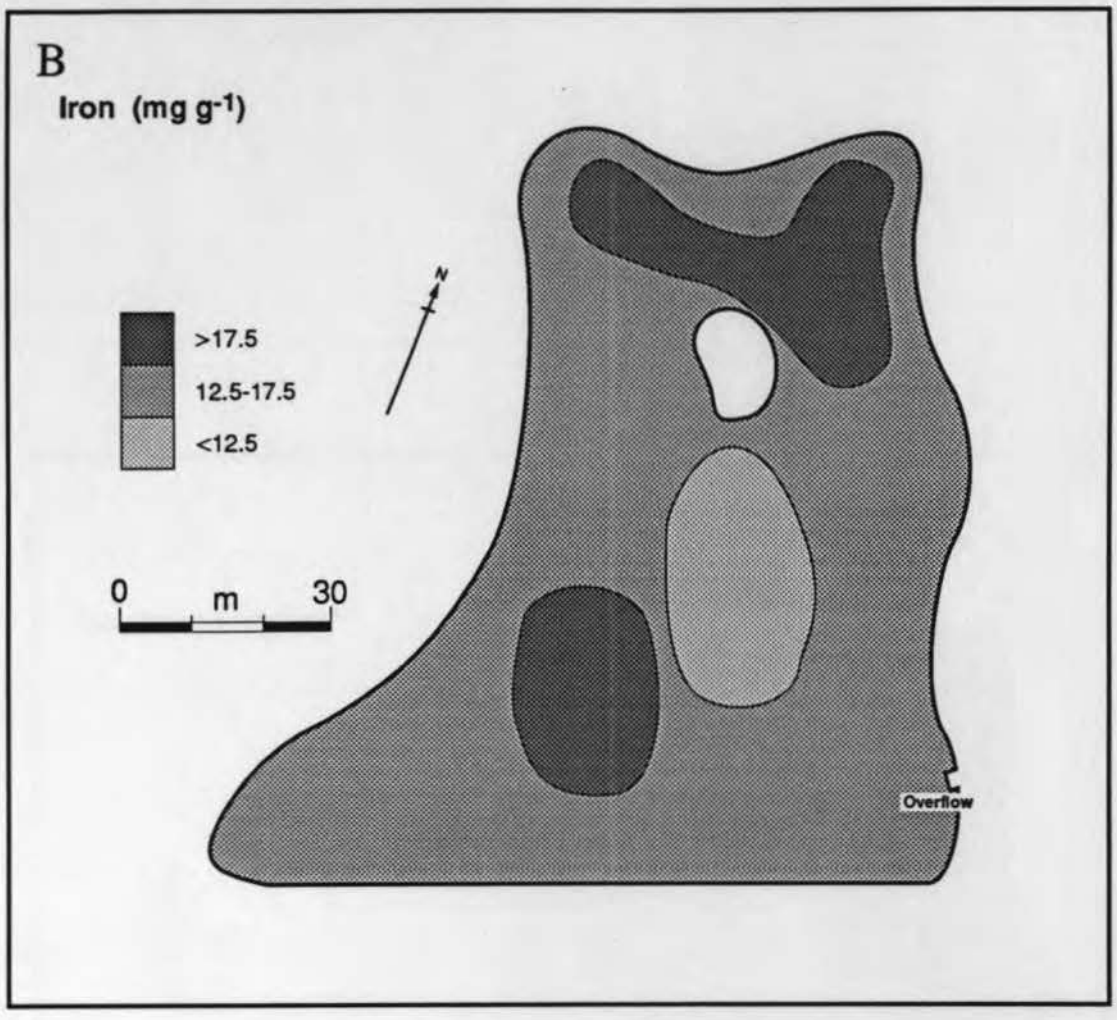
Fe and Mn (Fig 4.12 b and c) show similar trends with a decrease in concentration at about the boundary between the gyttja and the red clay in each core followed by a rise within the red clay to a concentration above that of the surface sediment samples. Once again the samples at 8 cm and 34 cm in core M10 show a trough and a peak respectively in Fe concentration and, although this is paralleled in Mn concentrations, it is not as pronounced within the range of values recorded. Fig 4.12 d gives the Fe / Mn ratio from each core. The ratio fluctuates in the cores between 20 and 100, with the highest average ratio shown by core M8 and the lowest generally in core M10. Each core exhibits fluctuations within the gyttja which cannot be correlated between cores. The ratio does, however, tend to rise upon sampling the red clay which indicates a deficiency in Mn. Core M10 shows the greatest fluctuation in the Fe / Mn ratio, possibly indicating changing redox conditions which may have been associated with mobilisation of heavy metals. However, profiles for the other three cores analysed do not show such variability so the evidence for heavy metals release in the past throughout the lake is inconclusive.

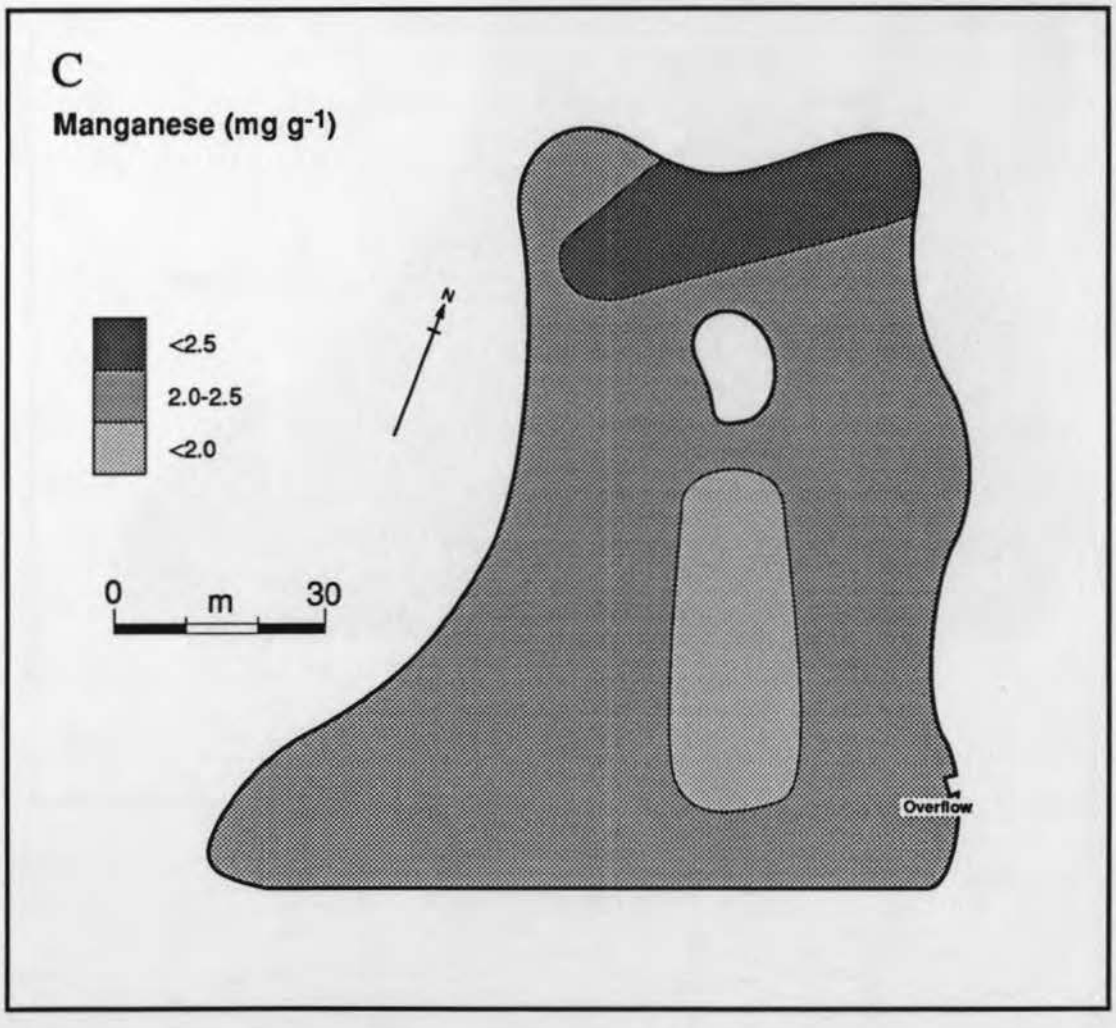
b. Spatial variability in the upper 1 cm of sediment

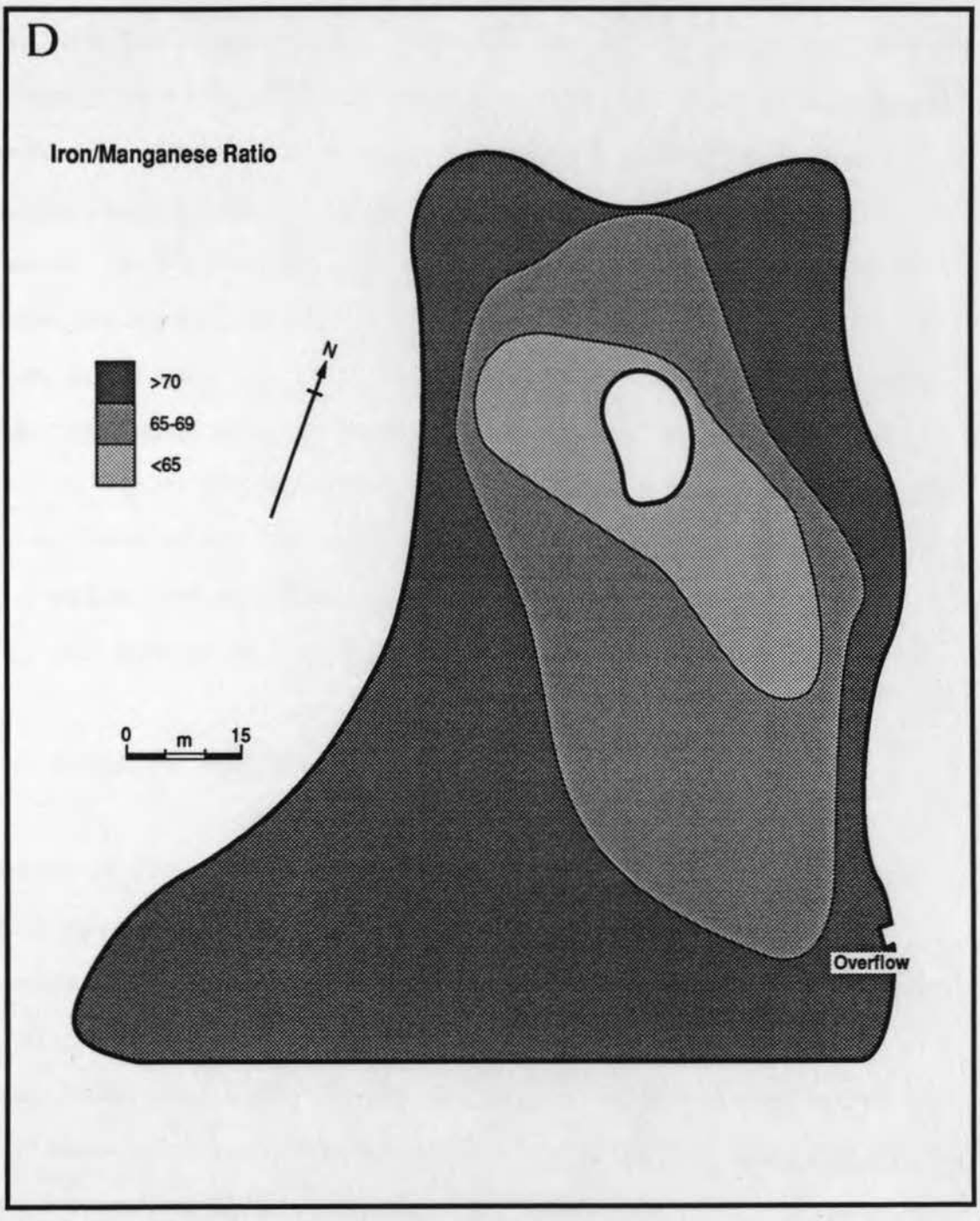
The spatial distribution of P in the upper 1 cm slice of lake sediment (Fig 4.13 a) varies from a maximum of 940 $\mu g\ g^{-1}$ in the south to a minimum of less than 250 $\mu g\ g^{-1}$ in the

Fig 4.13 Spatial distribution of P, Fe, Mn and Fe / Mn in the surface sediments of Swanswell Pool
a. P
b. Fe
c. Mn
d. Fe / Mn




B
Iron (mg g-1)
>17.5
12.5-17.5
<12.5
N
0
m
30
Overflow


C
Manganese (mg g-1)
<2.5
2.0-2.5
<2.0
N
0
m
30
Overflow


D
Iron/Manganese Ratio
>70
65-69
<65
N
0
m
15
Overflow

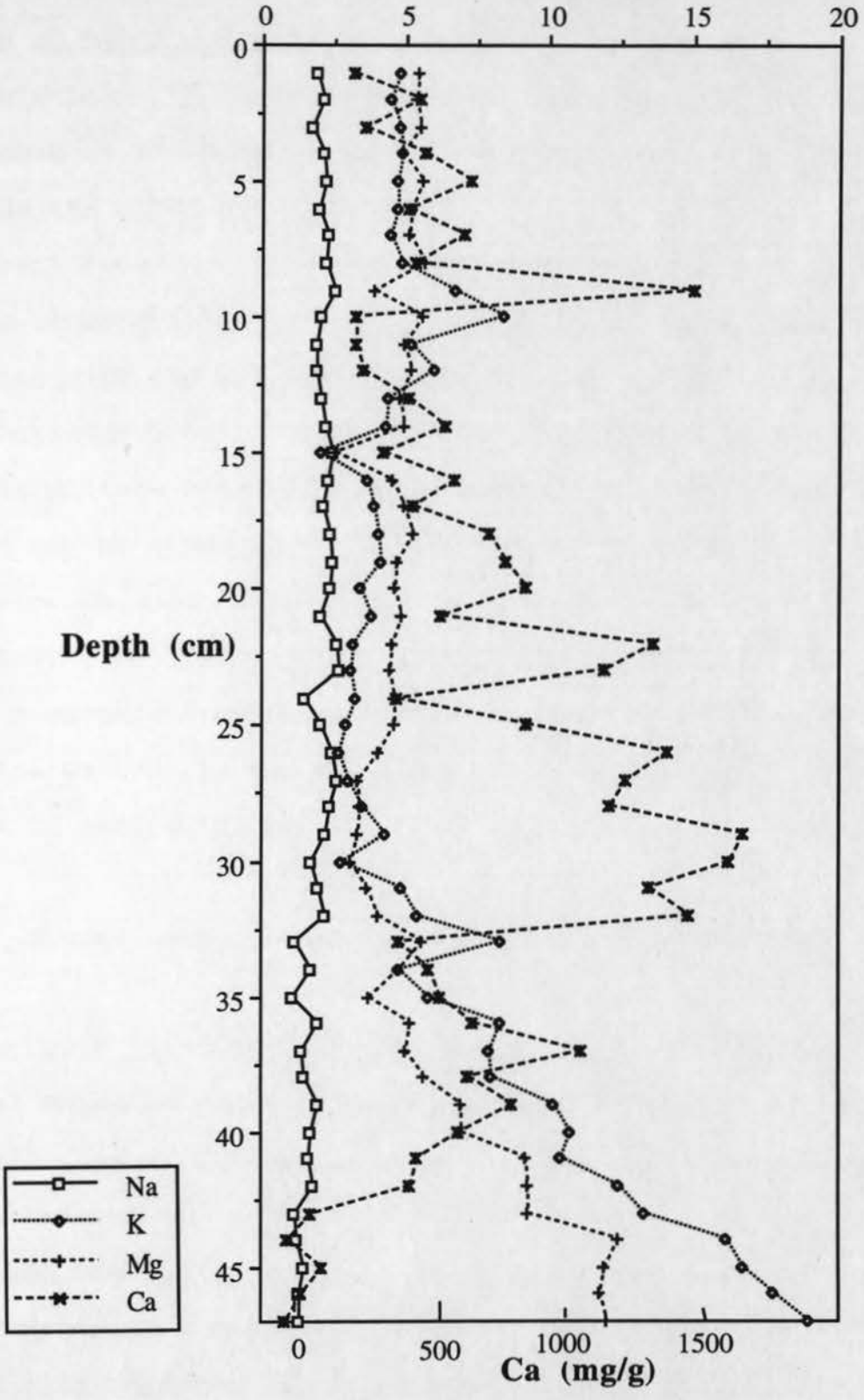
northeastern corner and in the south near the dam wall. A second peak in concentration occurs to the east of the island at 800 $\mu g\ g^{-1}$. The general trend is for decreasing concentrations towards the margins of the lake, particularly in the south and northeast.

Fe and Mn (Fig 4.13 b and c) are both low to the south of the island and high in the north of Swanswell Pool, but the Fe / Mn ratio (Fig 4.13 d) is lowest around the island and higher towards the edges of the Pool, perhaps indicating greater reducing conditions in relatively shallower water. Mitsch & Gosselink (1993) relate redox conditions to the presence of oxygen-consuming and oxygen-producing organisms and mixing of surface waters by wind and convection currents. The presence of shallow water and possibly disturbed and shallow sediment (Fig 4.2) would not provide suitable conditions for plants to root. A combination of this and the shelter offered by the island walls and concrete pool banks would ensure minimal mixing and hence, reduction of the underlying lake sediment.

3. Non-metallic elements

Results from the analysis of Na, Mg, Ca and K from core M10 are presented in Fig 4.14. Na shows a decrease in concentration downcore from 2000 $\mu g\ g^{-1}$ in the upper sample to 1100 $\mu g\ g^{-1}$ at the bottom of the core. Mg and K exhibit similar behaviour with little variation down to a depth of 30 cm followed by a marked rise to the base of the core. There is a peak in the concentration of Ca at a depth of 9 cm, where the peak in the heavy metals also occurred. The Ca trace is

Fig 4.14 Downcore trends in non-metallic elements Na, K and Mg (mg/g)



Red clay / black gyttja boundary, M10 = 34 cm

highly variable, but the general trend is for an increase downcore until the boundary with the red clay at between 33 and 35 cm depth where there is a marked decline in concentration with increasing depth. This decline is followed by a peak at 37 cm below which its concentration declines towards the bottom of the core.

Apart from Ca, there does not appear to be great variation in the concentration of the non-metallic elements until the junction with the red clay. This reflects little change in sedimentation both in terms of source and delivery. The Ca profile differs from the other three non-metallic elements, but it may be connected to metabolism by organisms such as snails or Ca-depositing algae. Comparison of Fig 4.14 with Fig 4.4 shows some similarities between the incidence of snail and *Chara* remains and the Ca profile. It is probable, therefore, that the Ca profile reflects cycling by biota rather than any change in sedimentation.

4.2.5 Mineral magnetic properties of the lake sediment

Chapter 2.10 ie) discussed the main reasons for obtaining the mineral magnetic characteristics of lake sediments to trace pollution history. These were for correlation of a grid of cores, tracing the sources of sediment to the lake and to establish whether it would be possible to use magnetic measurements as a surrogate for heavy metals analysis. The latter will be addressed in section 4.3a iii, but the rest of

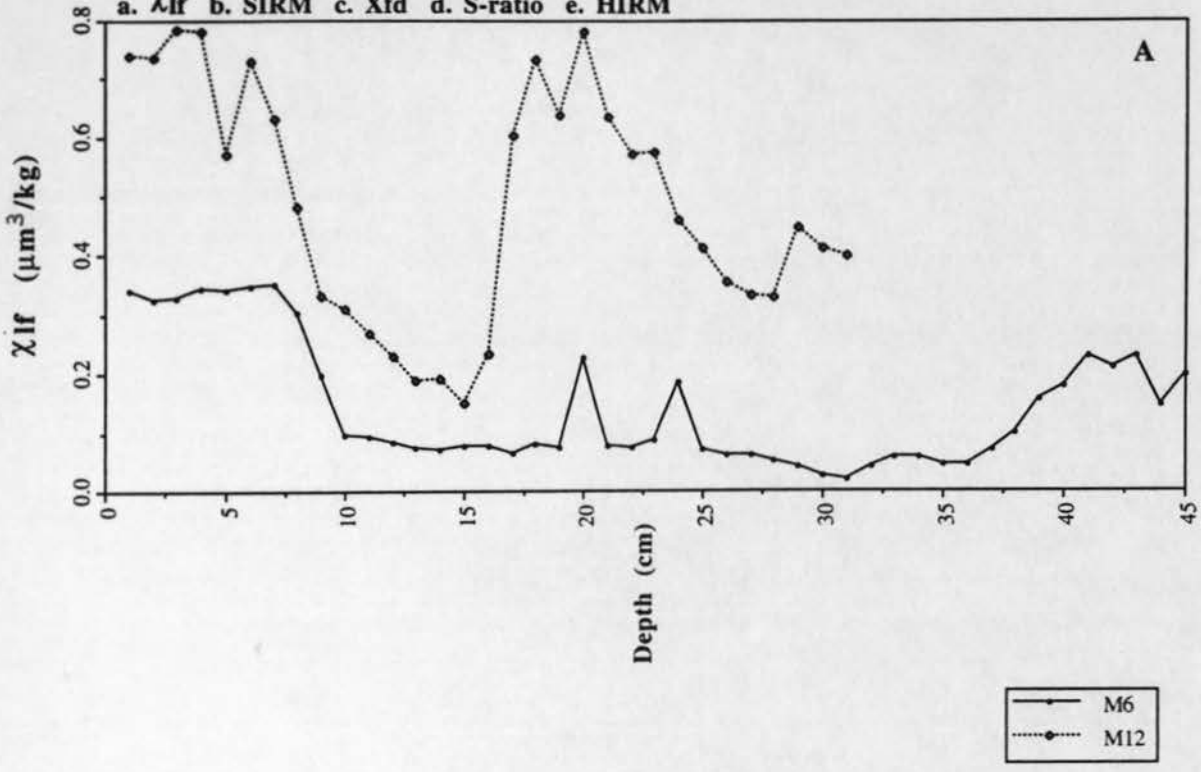
this section will be divided into three subsections. The first will describe the results obtained. This will be followed by an application of those characteristics to a matrix of χ_{lf} and SIRM profiles representing the grid of cores and an attempt to use these to correlate across the lake. Lastly, mineral magnetic characteristics will be used to resolve the changing nature of the sediments through time.

a. The mineral magnetic characteristics of the lake sediments

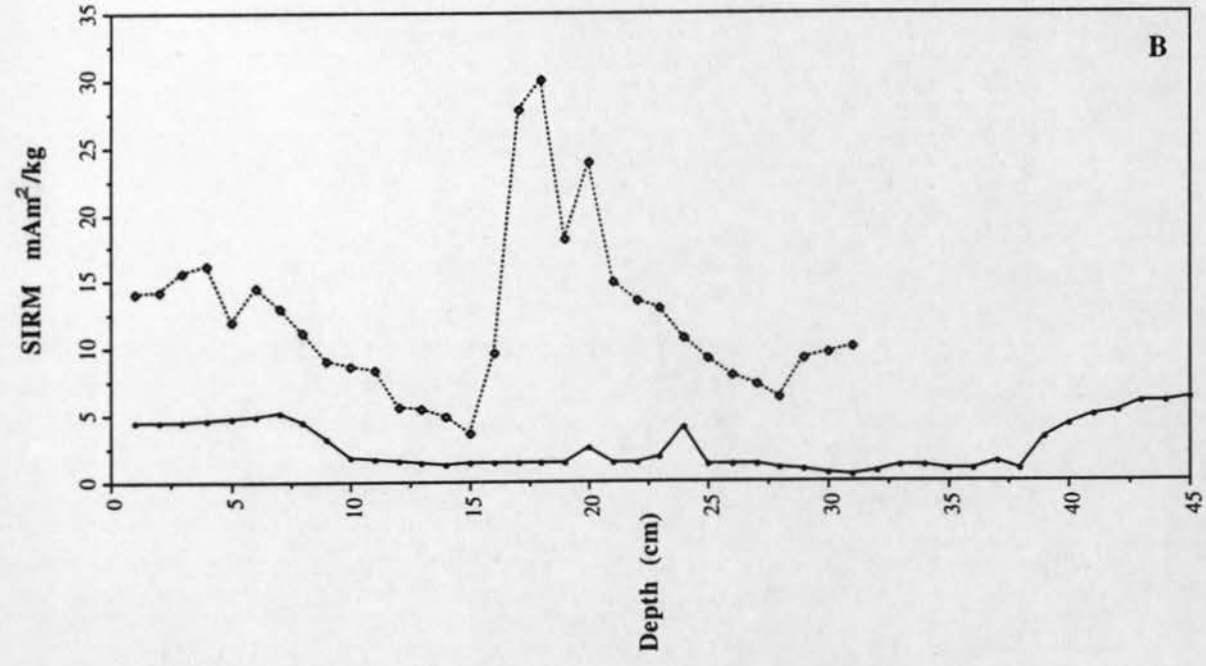
Figs 4.15 a and 4.15 b show traces for χ_{lf} and SIRM respectively for cores M6 and M12. The highest values for χ_{lf} in both cores are found in the top 10 samples, this is followed by a trough of lower values. There are two peaks in both cores at depths of between 20 and 24 cm where values of χ_{lf} are over 7.5 $\mu m^3\ kg^{-1}$. Values rise in both cores at the junction with the red clay. SIRM profiles are similar to those of χ_{lf} with high values in the uppermost sediments, a central peak at about 20 cm depth, and the junction with the red clay is indicated by markedly higher values in the case of core M6, and slightly higher values in core M12.

Values of χ_{fd} (Fig 4.15 c) for both cores fluctuate around the limits of detection. The upper 9 cm of core M6 has a maximum χ_{fd} of 50 $nm^3\ kg^{-1}$, whilst core M12 reaches 15 $nm^3\ kg^{-1}$ at a depth of 2 cm. There would therefore appear to be little or no input of magnetic minerals of a pedogenic origin

Fig 4.15 Mineral magnetic characteristics in lake sediments
a. χ_{lf} b. SIRM c. Xfd d. S-ratio e. HIRM

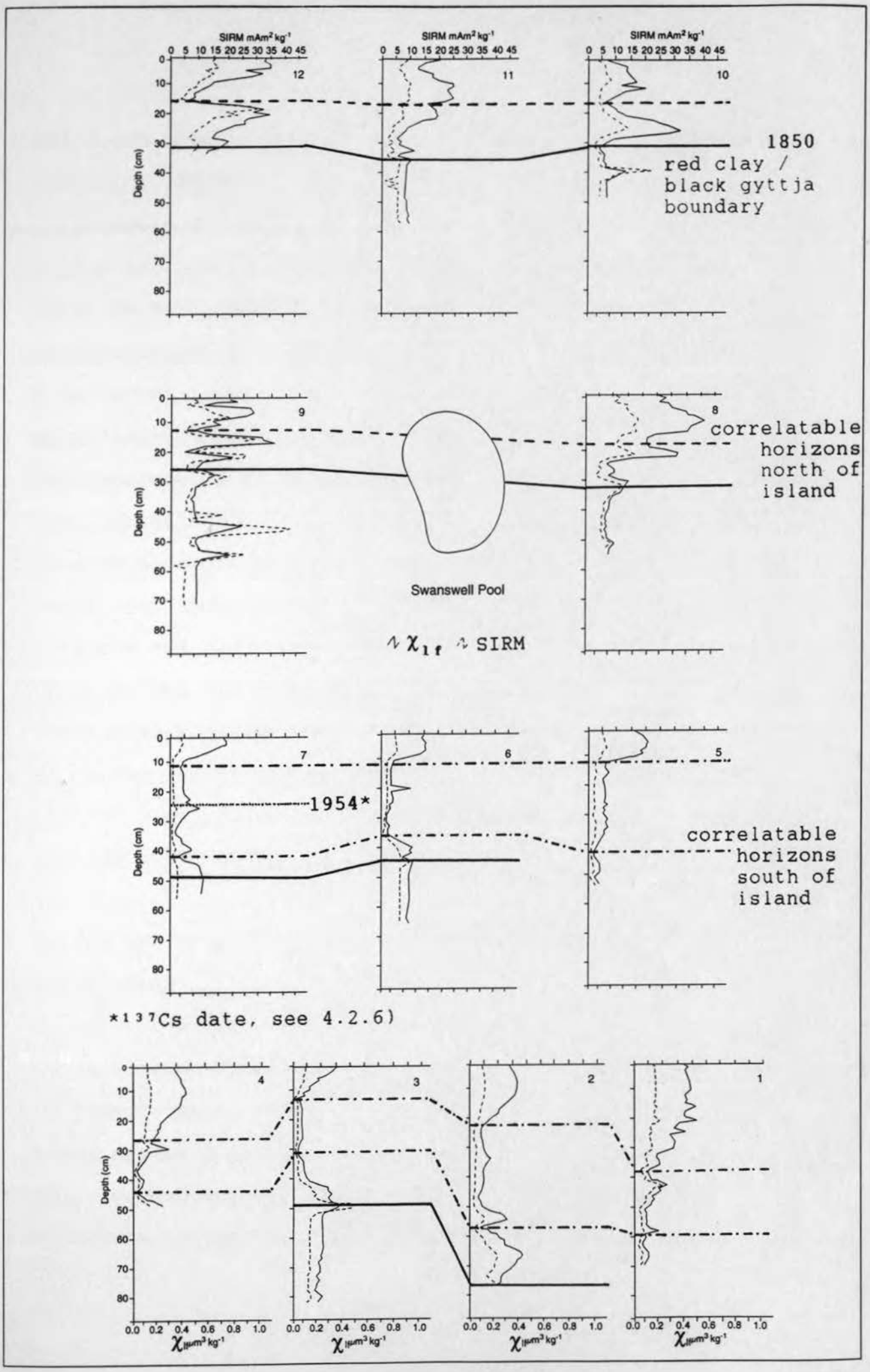


Red clay / black gyttja boundary
M6 = 45 cm, M12 = 31 cm



Red clay / black gyttja boundary
M6 = 45 cm, M12 = 31 cm

Fig 4.15 f Matrix of χ_{lf} and SIRM for all lake cores



which are usually characterised by high χ_{fd} (Thompson & Oldfield, 1986).

S-ratio and HIRM profiles are presented in Figs 4.15 d and 4.15 e and are mirror images of one another. The S-ratio reflects ferrimagnetic mineralogy and HIRM reflects canted antiferromagnetic mineralogy. The trace for the S-ratio, with high values in each core, (between 0.6 and 1.0) indicate a high ferrimagnetic component, possibly magnetite. The maintainence of these high values to the junction with the red clay indicates that the source of the gyttja probably has not changed through time. The values for HIRM in core M6 are much lower than those of M12, but vary little until the junction with the red clay when values rise to over 1.5 $mAm^2\ kg^{-1}$ from 38 cm to the red clay boundary. The HIRM trace for M12 fluctuates markedly from low values in the topmost samples to 17 cm where HIRM reaches 3 $mAm^2\ kg^{-1}$. Values decrease until the red clay boundary where HIRM begins to increase, reaching 2.3 $mAm^2\ kg^{-1}$ at 32 cm.

b. The use of a matrix of χ_{lf} and SIRM profiles in core correlation

A matrix to show χ_{lf} and SIRM profiles throughout the grid of lake cores is presented in Fig 4.15 f. On the basis of these magnetic properties, the lake can effectively be divided into two sub-basins, with the profiles in the northern transects exhibiting marked fluctuations in both SIRM and χ_{lf};

more particularly within the upper black gyttja. The two transects in the southern half of the pool exhibit profiles which are less variable. The profiles within the red clay also tend to exhibit little variation, with the exception of core M9 in which there are three peaks common to both parameters at depths of 40, 45 and 54 cm.

The boundary between the red clay and the black gyttja is characterised by a peak in both magnetic parameters in all cores except core M7. The largest peak in χ_{lf} at this boundary is in core M12.

Maximum χ_{lf} values of up to 0.9 μm^3 kg^{-1} in the upper sediments are found in the northern sub-basin. The highest values in the south are slightly more than half of those in the north, reaching a maximum of 0.48 μm^3 kg^{-1} in core M5.

Highest SIRM values parallel those of χ_{lf}, with the largest values recorded in the sediments in the northern sub-basin. The highest value in the upper sediments approaches 30 Am^2 kg^{-1} in core M9 at a depth of 14 cm, the highest value to the south, apart from those found near the red clay boundary is 9 Am^2 kg^{-1} in core M1 at a depth of 21 cm.

Correlation between the magnetic traces for cores along the two transects in the north of the Pool is fairly clear, as is that between the cores along the two transects in the south of the Pool. It is not possible to match the profiles obtained in the northern transects with those in the south on the basis of magnetic characteristics alone, apart from correlating from

north to south using the visible stratigraphies (Fig 4.3 and 4.4).

The correlatable feature in the northern sub-basin is a trough in both SIRM and χ_{lf} below the high values in the upper sediments. There is also a peak in both magnetic parameters associated with the boundary between the red clay and the black gyttja. The trough in the black gyttja overlies a peak, which is not associated with the red clay boundary peak. Core 12 exhibits a double peak just above the red clay boundary. There are peaks in the red clay in cores M8, M9 and M12, which may be synchronous, but it is not possible to extrapolate between the cores as the relationship is inconsistent.

In the southern cores there are two locations in the profiles where correlation is possible. The upper few samples exhibit higher SIRM and χ_{lf} values and at the point these values decline sharply, a time synchronous correlation may exist. Below this horizon is a plateau of unvarying values terminated by a single or double peak; a second correlatable feature. Below this peak, values become more variable with most of them increasing. However in cores M1, M4 and M5 SIRM and χ_{lf} generally decrease.

Difficulties in correlation are encountered in the cores located around the margins of the pool. In a small water body such as the Swanswell Pool the majority of the cores are near the banks where they may be disturbed. Cores M6, M2 and M3 probably represent the least disturbed cores from the suite and consequently show similar profiles with least variation.

It is noticeable that those cores taken from the marginal areas of the pool with the shallowest depths of water and sediment offer the least convincing correlatable horizons.

c. Mineral magnetic characteristics as an indicator of changing sediment source with time

Subsection a.) mentioned the use of χ_{fd} values in identifying sediment sources, as the low values indicated a lack of magnetic minerals of pedogenic origin. The high and consistent S-ratio suggests no change in the source of the gyttja. To specifically apply mineral magnetic measurements to assess whether sediment source has changed with time, scattergrams of χ_{lf} against SIRM were used. This ratio can be used as a guide to magnetic particle size (Thompson & Oldfield, 1986) and also reflects magnetic mineralogy in the sample. Fig 4.16 presents data kindly provided by J A Lees (Geography Division, Coventry University) showing the division of a scattergram of χ_{lf} and SIRM into lines of gradient characteristic of materials such as polluted road dusts, synthetic magnetic materials and natural sediments from rivers and soils.

Scattergrams of χ_{lf} against SIRM in the lake sediment cores are presented in Fig 4.17. Two distinct trends on each graph can be seen; a low SIRM/ χ_{lf} ratio corresponding to the black organic gyttja, which is more ferrimagnetic, and has a high SIRM/ χ_{lf} ratio corresponding to the red clay and indicating a trend towards a canted antiferromagnetic mineralogy.

Figure 4.16: SIRM/χlf ratios for sets of polluted materials
(unpublished data, J A Lees)

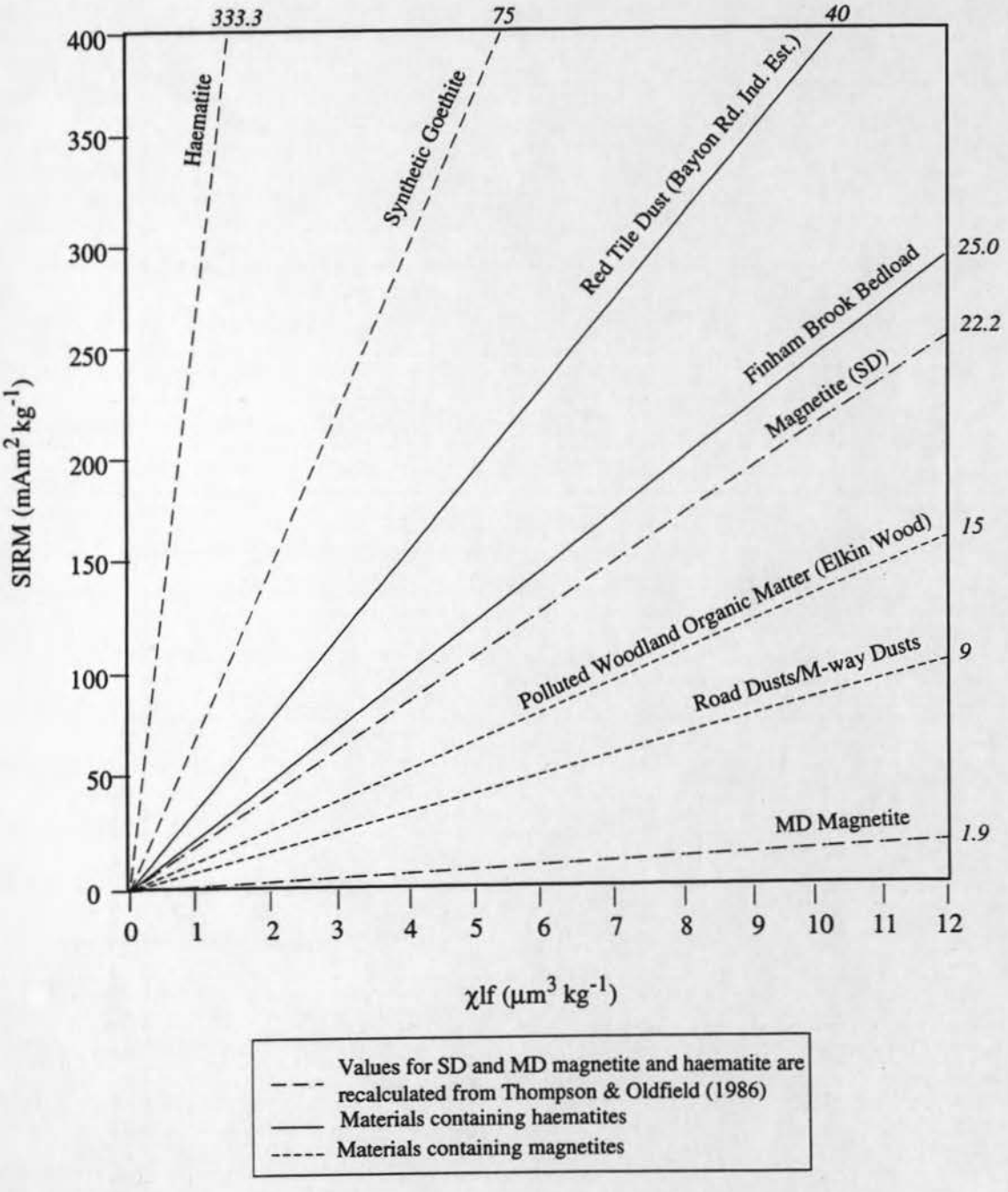
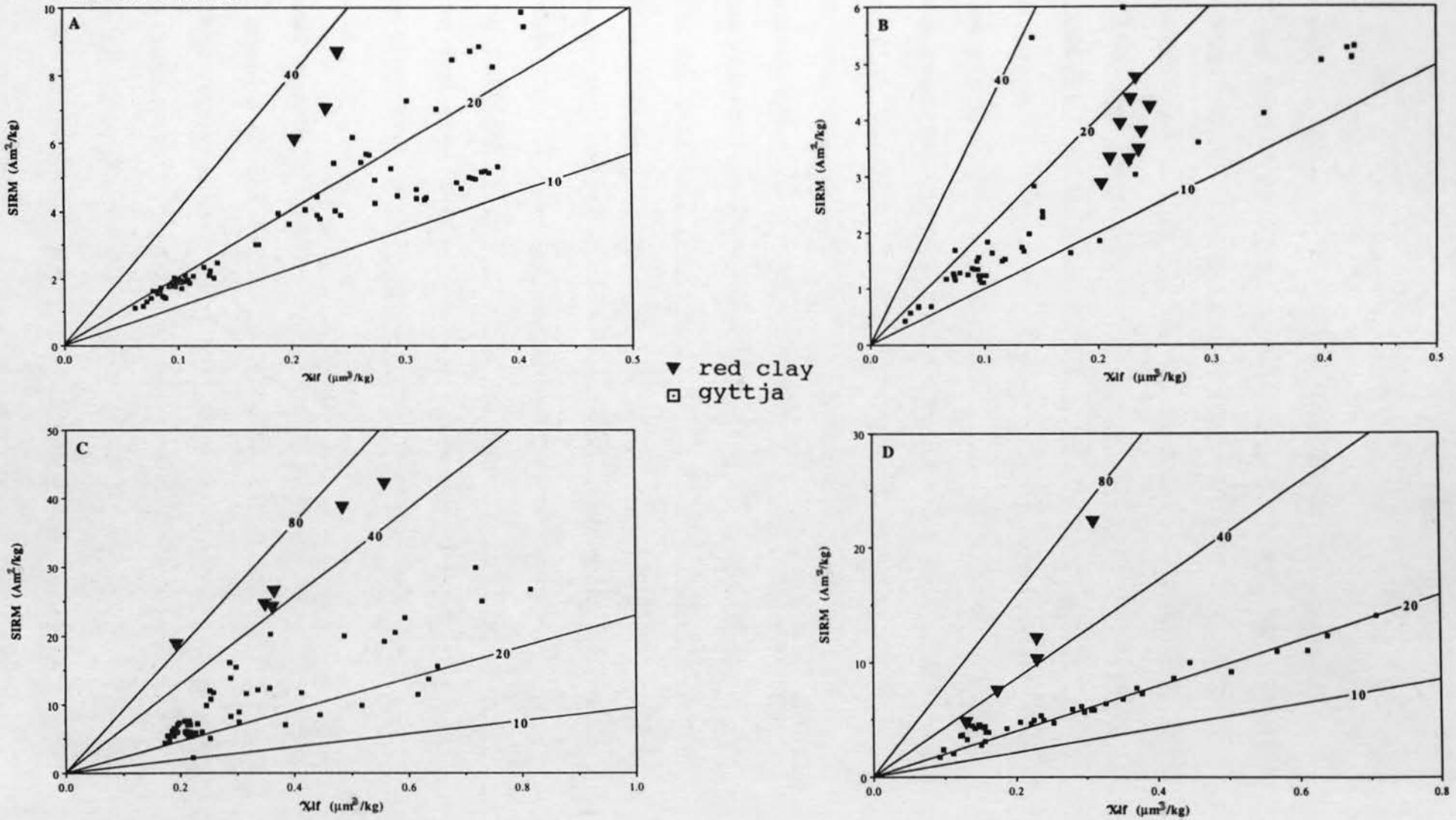


Fig 4.17 Scattergram of χlf against SIRM for lake sediment cores
a. M2 b. M7 c. M9 d. M10



Superimposed on these scattergrams are lines of gradient representing ratios of 1:10, 1:20, 1:40 and 1:80. The majority of the gyttja plots between ratios of 10 and 40. Decreasing ratios indicate an increasingly ferrimagnetic mineralogy, such as magnetite, and increased magnetic grain size. Increasing ratios indicate an increasing canted antiferromagnetic component, such as haematite. Core M2 is the longest of the four cores plotted with 79 samples (Fig 4.17 a). The samples can be resolved into several different groups relating to their position in the core. From the basal sediments to the uppermost samples, the low ratio indicates increasing ferrimagnetic minerals, such as magnetite, and increasing grain size, which may be indicative of an increasing proportion of particulate pollutants which are ferrimagnetic multidomain grains (Thompson & Oldfield, 1986 and Fig 4.16). Whilst cores M7, M9 and M10 do not show this resolution, the general trend of increasing antiferromagnetic minerals and decreasing ferrimagnetic minerals is present, the samples within the red clay indicating the gradual change in sediment source as they lie on a different line of gradient to the gyttja.

Mineral magnetic measurements therefore show the change in sediment source at the boundary between the red clay and the black gyttja and the dominance of pollution particles in the uppermost sediments of Swanswell Pool commensurate with the dominance of atmospherically derived sources to the sediment. However, use of magnetic properties to fingerprint the cores

of a small urban lake with a complex history is problematic. The question of the application of magnetic measurements to both Swanswell and Wyken Pools was addressed by Foster & Charlesworth (1994). The following paragraph comments on Swanswell Pool; Wyken Pool is covered in Chapter 5.2.5.

Table 4.6 gives the coefficient of variation (CV) at two standard deviations (95%) for various properties of the surface lake sediment samples and for one core at Swanswell Pool. In the case of the mineral magnetic characteristics, the spatial variability is similar to or less than that of the downcore variability which indicates that in general mineral magnetic properties may reflect the characteristics of the lake such as sorting processes, the presence of magnetotactic bacteria (Fassbinder *et al.*, 1990; Mann *et al.*, 1990) or greigite (Snowball & Thompson, 1992) as much as trends through time. The CV for heavy metals, however, is much higher downcore than spatially which indicates that the core may provide a reasonable representation of trends in pollution history in Swanswell Pool.

4.2.6 Dating using ^{137}Cs and ^{210}Pb

In order to put the history of heavy metal pollution in Swanswell Pool into an historical context, one lake sediment core was subjected to radioisotope dating as outlined in Chapter 2.12. The results are presented in 2 subsections which will discuss ^{210}Pb and ^{137}Cs separately.

Table 4.6 Coefficient of Variation at 2 standard deviations (95%) for surface sediments and a lake sediment core from Swanswell Pool. From Foster & Charlesworth (1994)

	Surface samples n=12	Core n=72
DBD	120.0	71.1
χ_{lf}	75.4	150.4
SIRM	100.3	121.0
IRM	129.7	170.7
S-ratio	24.7	200.0
HIRM	100.0	396.2
Pb	44.6	112.2
Cu	72.1	135.2
Ni	55.5	111.6
Zn	66.1	206.8
Fe	41.9	125.1
Mn	131.2	83.5

DBD = dry bulk density

Results of the analysis undertaken in the Physics department at Coventry University are presented in Table 4.7 a and Fig 4.18.

i. ^{137}Cs

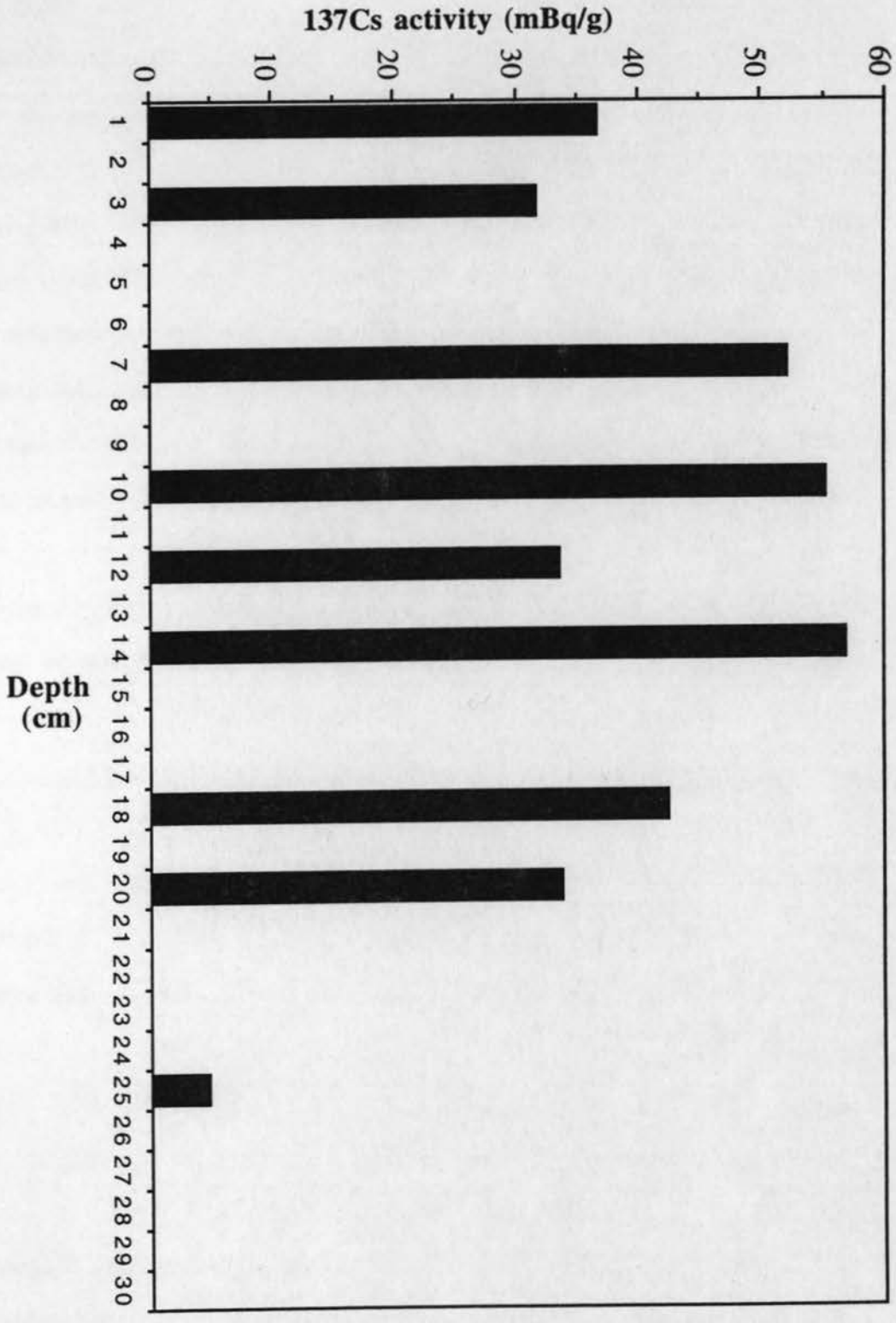
^{137}Cs activity is below the limits of detection of the instrument by 27cm depth. There is a large percentage error at 25 cm and a low activity which strongly suggests that 25-27 cm depth in core M7 could therefore represent 1954. This gives a sediment accumulation rate in the last 39 years of 0.625 cm yr^{-1}. The red clay in core M7 is reached at a depth of 48 cm. The intervening 21 - 23 cm, therefore, represent the sediment accumulated between 1850 and 1954; a sediment accumulation rate of 0.221 cm yr^{-1}. However, as sediments accumulate, they are compressed, as illustrated by bulk density data (Fig 4.6) in that the upper sediments have a lower bulk density than those towards the base of a core. Taking this into account, the equivalent depth of sediment can be calculated using dry bulk density. The upper 26 cm, if the same bulk density as those sediments below, would occupy 18.54 cm, some 6.5 cm less. The accumulation rate for the sediments since 1954 can therefore be corrected to 0.4635 cm yr^{-1} using ^{137}Cs as a means of dating.

Table 4.7a Activity of ^{137}Cs and ^{210}Pb in core M7 from Swanswell Pool (mBq g^{-1}).

Depth (cm)	Total ^{137}Cs	% error	Total ^{210}Pb	Supported ^{210}Pb	Unsupported ^{210}Pb	% error
2	36.6	35	190.0	4.4	185.6	52
3	31.8	30	168.1	2.4	165.8	55
7	52.1	30	188.4	4.4	184.0	40
10	55.2	25	121.6	4.0	117.6	50
12	33.6	30	81.3	3.0	78.3	50
14	57.0	25	96.1	4.5	91.6	50
18	42.4	25	61.1	2.4	58.6	42
20	33.8	30	73.9	3.9	69.9	46
25	4.8	65	32.6	2.2	30.4	60
27	ND	ND	ND	ND	ND	ND
30	ND	ND	ND	ND	ND	ND

Where ND = not detectable

Fig 4.18 Downcore 137Cs activity in core M7 (mBq/g)



ii. ^{210}Pb

Unsupported and supported ^{210}Pb appear to be below the limits of detection by 25-27 cm depth. However, the unsupported ^{210}Pb levels are very high in the upper samples in comparison with the supported ones. Table 4.7b compares ratios of surface activities from Swanswell with those from Merevale Lake and Seeswood Pool (unpublished data kindly provided by I D L Foster, Geography Division, Coventry University) both Merevale and Seeswood Pools are rural lake catchments in the English Midlands (Foster *et al.*, 1987a).

Table 4.7 b ^{210}Pb activities from Swanswell Pool compared with those from other Midland England lakes.

	1	2	3
a) Total	190.0	159.7	64.8
b) Supported	4.4	38.1	31.1
c) Unsupported	185.6	121.6	33.7
b:c	42.2	3.2	1.1
a:c	0.98	0.76	0.51

1 = Swanswell Pool

2 = Merevale Lake

3 = Seeswood Pool

It is apparent that the total ^{210}Pb in the surface sample at Swanswell Pool is considerably higher than that at Merevale or Seeswood, and that the proportions of total : unsupported, and supported : unsupported are also very different. As explained in Chapter 2.12 i, the unsupported component of the ^{210}Pb measured is from direct atmospheric sources, indirect atmospheric sources (via the catchment in re-eroded soils, channel banks etc) and radon decay in the water column (Oldfield & Appleby, 1984). However, the principal source of unsupported ^{210}Pb is generally accepted to be directly from the atmosphere with the indirect and water column sources contributing very little to the total inventory (Oldfield & Appleby, 1984). The ratios in Table 4.7 b emphasise the dominance of atmospherically derived ^{210}Pb at Swanswell Pool. Of the total ^{210}Pb, 98% is unsupported, and the ratio of unsupported to supported is 42.2, almost 15 times that at Merevale and 40 times that at Seeswood.

An average estimate of the mean annual deposition rate of unsupported ^{210}Pb from direct fallout from the atmosphere has been estimated at 0.35 pCi cm^{-2} yr^{-1} (P Appleby, pers comm). This is close to published values from average flux rates calculated from lake sediments of 0.55 pCi cm^{-2} yr^{-1} (Oldfield & Appleby, 1984). Converting these values to mBq cm^{-2} yr^{-1} so that they are comparable with those obtained for Swanswell Pool, the mean annual deposition rate would be between 12.95 and 20.35 mBq cm^{-2} yr^{-1}. The dry bulk density for the top sample of M7 from Swanswell Pool is 0.185 g cm^{-3} (Fig 4.6) and

the accumulation rate calculated for the sediments from 1954 to the present day based on the ^{137}Cs date is 0.4635 cm yr^{-1}. The annual deposition rate for Swanswell Pool is therefore:

185.6 mBq g^{-1} (Table 4.7 a) x 0.185 g cm^{-3} x 0.4635 cm yr^{-1} =

15.92 mBq cm^{-2} yr^{-1}

The total ^{210}Pb in Swanswell Pool is therefore directly comparable with other published data.

^{210}Pb activity does not register below 25 cm in core M7. Many reasons are postulated in the literature for an incomplete profile and these are discussed in Chapter 2.12 i, and, as applied to Swanswell Pool, these include:

1. Migration of ^{210}Pb in the sediment column. Smoothing of the curve would be expected in the upper 10 cm due to bioturbation, but the ^{210}Pb does not register below 25 cm, so whilst bioturbation may be reponsible for some movement in the upper sediments, this does not explain the lack of this radioisotope in the lower ones. Some mobilization of ^{210}Pb may occur in pore water, but according to Eakins (1983) there is indirect evidence that this process is minimal due to sharp peaks in some profiles which would be smoothed if migration had occurred.

2. The flux of ^{210}Pb should be constant. This cannot be guaranteed in urban lakes whose catchments are characterised by disturbance. However, in the case of Swanswell Pool, there has been no catchment, apart from a small park, since 1850 (Chapter 3.4.1) and sediment is derived from the atmosphere or is autochthonous in origin. Bulk density, loss on ignition and heavy metal profiles give no evidence of change in sediment delivery regime at the site, so it is to be assumed that the flux of ^{210}Pb has been reasonably constant over time.

3. The residence time of ^{210}Pb in the atmosphere is constant. Oldfield & Appleby (1984) admit that whilst the relationship between input and fallout is not conclusive, it is a good approximation. Calculations presented above show that the annual accumulation rate of ^{210}Pb in Swanswell Pool is comparable with calculated values of atmospheric flux so it is likely that the input of ^{210}Pb has been constant.

4. Sediment resuspension and focusing will lead to lowered levels at sites of active erosion and enhanced levels at sites of active deposition. Oldfield & Appleby (1984) suggest that a study should never rely on a single core, but should instead establish a chronology from a set of representative cores. Unfortunately, this was not possible in the duration of this study, but should provide the focus for future work.

The reason for the lack of ^{210}Pb below 25 cm is therefore not known, but it may be connected with sediment entrainment and focusing.

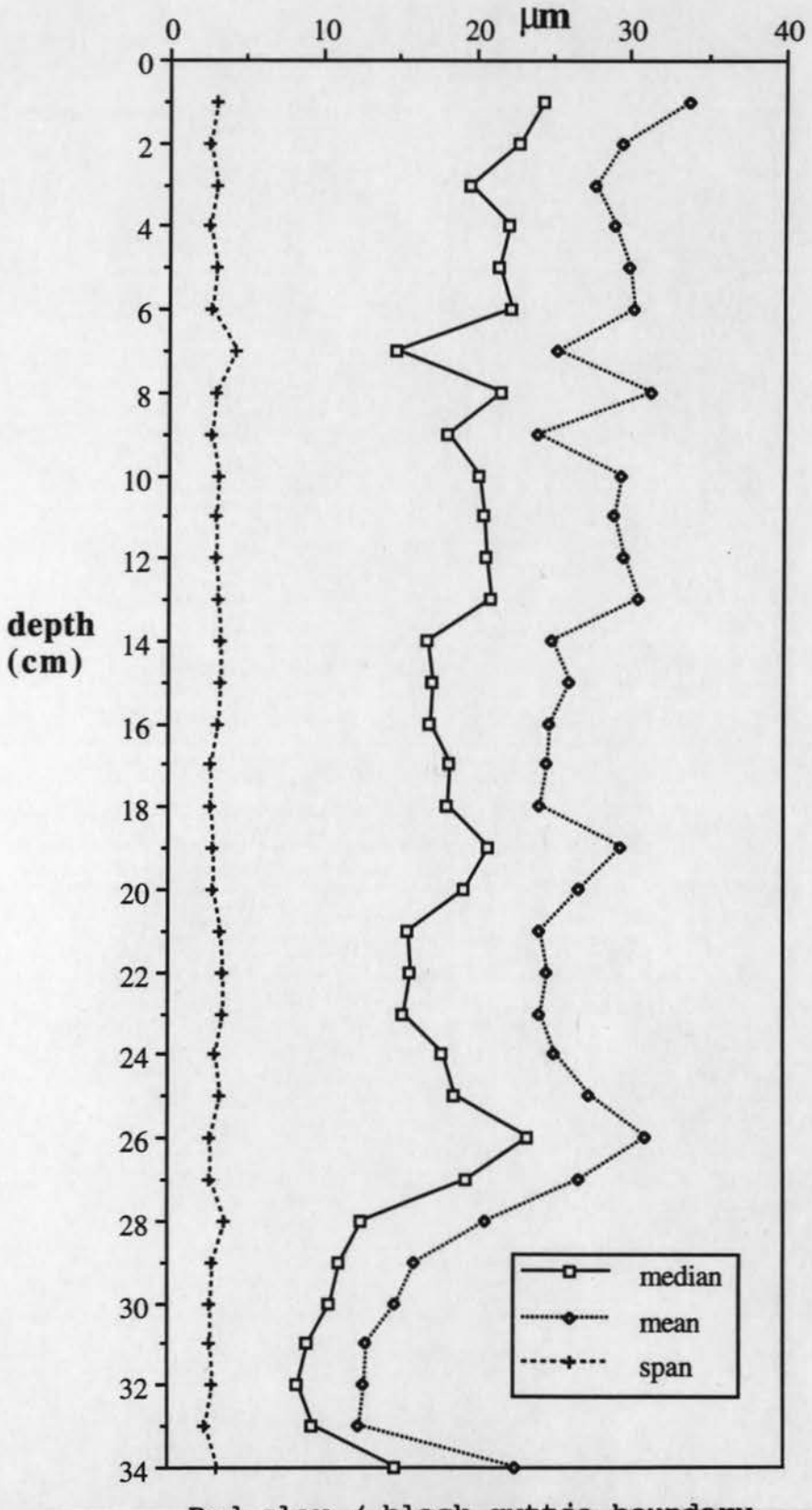
4.2.7 Particle size analysis

Particle size analysis was carried out on core M8 from Swanswell Pool. The core was chosen as it penetrated the red clay and there was sufficient sediment left to perform a particle size analysis after analysis of heavy metal content.

The mean particle size in core M8 (Fig 4.19) declines gradually with depth from 34 μm in the top sample to the boundary with the red clay where it decreases to 14.5 μm. A small peak below the boundary at a depth of 36 cm with a mean particle size of 26 μm, is followed by a further decrease to 16 μm in the basal sample of the core. Span is a measure of the spread of particle size about the average and is used to define sorting or dispersion of the sediment (Allen, 1990). Span (Fig 4.19) does not fluctuate greatly in core M8, where values range from about 2 to 4. The lower values are found in the red clay.

Examples of Laser Granulometer traces from individual samples showing the distribution of particle size are shown in Fig 4.20. The top 32 cm is generally characterised by multimodal distributions with up to 5 peaks, mainly dominated by the 25 μm fraction in the top 9 cm and the 20 μm peak from 10 cm to 25 cm. Below 25 cm, the dominant peak is at 10 μm.

Fig 4.19 Particle size distribution in core M8



Red clay / black gyttja boundary
M8 = 34 cm,

Where span is an index of sorting

Fig 4.20 Examples of the multimodal character of individual lake sediment samples

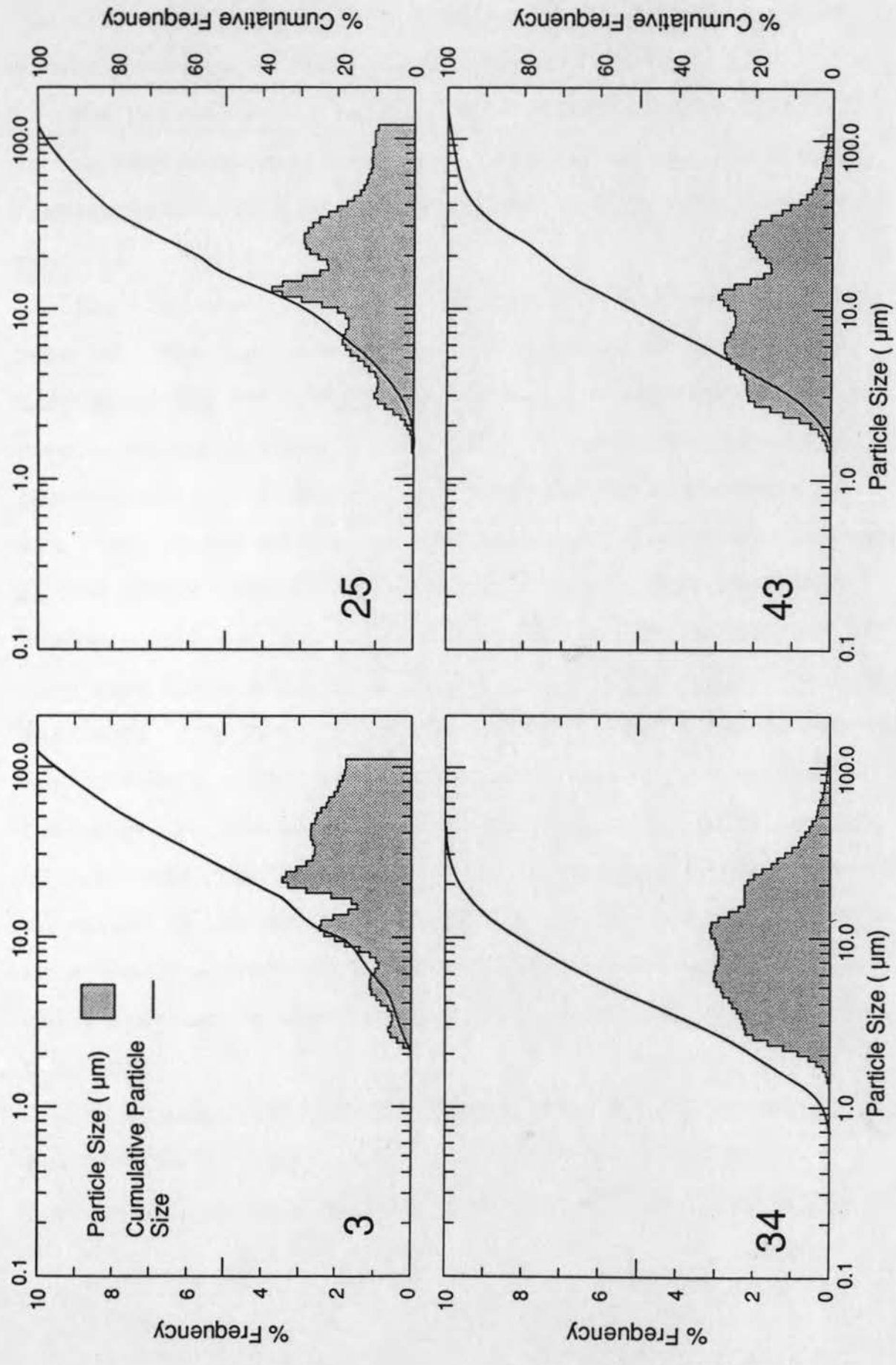


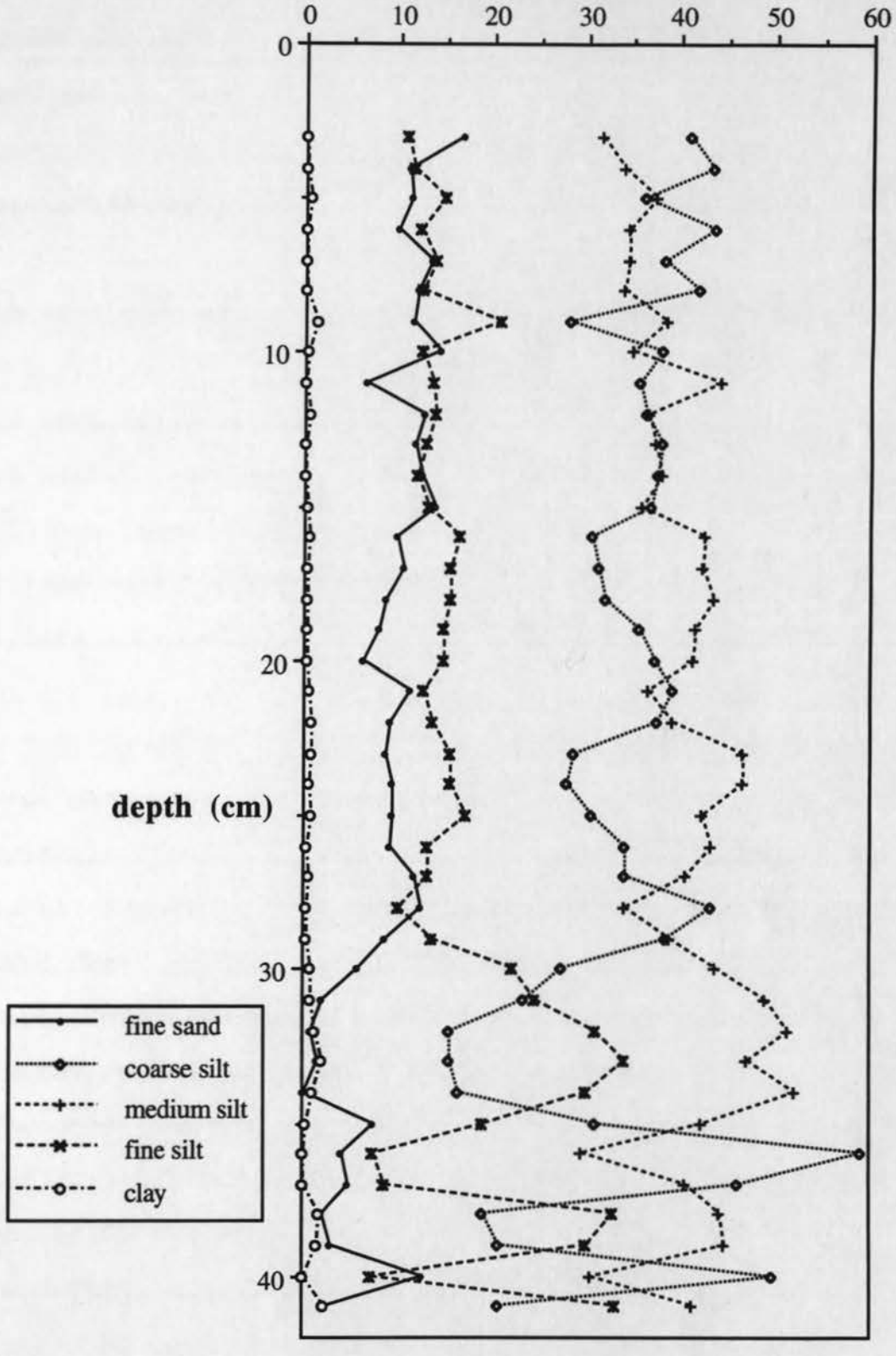
Fig 4.20 illustrates this multimodal characteristic with a gradual decrease in size of the dominant peak.

The tail above 100 μm indicates the percentage of grains in the fine sand range. However, 100% of all grains in the samples tested were below 118 μm; ie. mostly finer than fine sand.

Fig 4.21 shows the change in particle size with depth in core M8 . The clay fraction is less than 2% of the total throughout the core. The values for the other size fractions remain fairly constant in the upper 28 cm of the core. The proportion of fine sand in the upper sediments contributes 10%, that of the coarse silt 40%, and medium silt 31%. Changes in the proportions of particle sizes occurs just above the boundary with the red clay at about 31 cm. The percentage of fine sand falls to zero at 34 cm; rising slightly in the basal sediments. Fine and coarse silt appear to be mirror images of one another : a decline in the one is mirrored by a rise in the other. At the boundary with the red clay, the percentage of fine silt increases by 22%, the coarse silt declines by 20% to values of 34% and 18.5% respectively. Medium silt rises from 34% at a depth of 28 cm to a maximum of over 50% at 34 cm. The values of each fraction are highly variable below this boundary.

In general, the core is dominated by the medium silt fraction which contributes over 50% of the sediment, particularly at the boundary with the red clay. The trends of

Fig 4.21 % change in particle size with depth in core M8



medium and fine silt are identical. Until the boundary with the red clay, there does not appear to be evidence to suggest any great changes in sediment regime during the deposition of the gyttja.

4.3 Statistical analysis

Statistical analysis was carried out on a number of data sets:

The 12 lake cores separately
The 12 surface samples
The 12 lake cores together
The 4 lake cores with heavy metals data together
The 4 lake cores with heavy metals data separately

Table 2.21 shows the range of laboratory analyses carried out on these data sets. Descriptive statistics including skewness and kurtosis, as well as correlation analysis, were carried out on all the above data sets. Regression was carried out on selected data sets as explained in section 4.3a iii below. Principal Component Analysis (PCA) was carried out on the 4 lake cores with heavy metal data separately.

The objectives of statistical analysis were introduced in Chapter 2.13 and were mainly to identify whether particular properties of the sediments could be discriminated independantly, or whether they shared a high degree of

collinearity. In order to do this, statistical tests were applied to the 7 questions put forward in Chapter 2.13.

To ascertain whether the data was suitable for parametric statistical tests, they were subjected to a number of transformations and skewness and kurtosis values were computed. It was found that transforming the data did not consistently improve the distribution and that the raw data approximated a normal distribution. The raw data were therefore suitable for parametric tests.

Collinearity between mineral magnetic parameters and between heavy metals was determined using correlation. The use of magnetic measurements as a surrogate measure of heavy metals was investigated by means of regression.

PCA was used to reduce the number of variables to a set of dominant factors. As some variables appeared to load on more than one component, varimax rotation was carried out so that one variable would load highly on one component only. This effectively separated the variables into discrete clusters and enables determination of controlling factors.

The results of statistical analysis is divided into 2 subsections, firstly that covering descriptive statistics, correlation and regression, and secondly a description of the results obtained from PCA.

a. Descriptive statistics, correlation and regression

This is divided into four subsections in order to determine relationships between magnetic parameters and between the heavy metals. It also seeks to determine whether there is any relationship between heavy metals and mineral magnetic characteristics of the sediment and whether mineral magnetism can be used as a predictive tool in urban lakes. Lastly, the particle size characteristics of the lake sediment are compared with heavy metal concentrations to determine whether particle size might affect metal concentrations.

Table 4.8 gives a summary of the results from Swanswell Pool. Comparative tables which include Wyken Pool and Wyken Slough are presented and discussed in Chapter 6.

i. Relationship between mineral magnetic parameters in lake sediment cores and surface samples

Correlations between magnetic parameters highlight a high level of interdependance. Table 4.9 illustrates this with a correlation matrix taken from the sum of all the cores analysed in Swanswell Pool. With a critical R value for the correlation coefficient of 0.0815, correlations between measured parameters such as χ_{lf} and SIRM are consistently high. Correlations between derived parameters such as HIRM, χ_{fd} and the S-ratio are also highly significant.

Table 4.8 Summary descriptive statistics of the lake sediments from Swanswell Pool (n=156)

Variable	Mean	Minimum	Maximum
χ_{lf} [1]	0.29	0.0	1.0
χ_{fd} [2]	3.91	0.0	49.3
SIRM[3]	5.88	0.1	20.1
S ratio	0.71	0.2	1.0
HIRM[3]	0.77	0.0	5.4
DBD[4]	0.38	0.0	1.2
WBD[4]	1.29	0.6	2.5
DWR	0.29	0.0	0.6
Fe[5]	35.62	2.5	187.4
Mn[5]	1.13	0.1	3.5
Fe/Mn	56.53	28.8	102.8
Cd[6]	5.82	0.0	17.4
Pb[6]	198.93	0.0	553.8
Ni[6]	46.07	4.0	138.7
Zn[6]	1034.59	28.0	3642.1
Cu[6]	179.77	0.0	574.0
P[6]	325.24	12.0	1663.9
Na*[5]	2.15	1.4	2.6
K*[5]	4.21	2.0	8.4
Ca*[5]	81.08	31.7	166.6
Mg*[5]	4.58	2.5	5.6

* n=31

Units
[1] $\mu m^3\ kg^{-1}$
[2] $nm^3\ kg^{-1}$
[3] $mAm^2\ kg^{-1}$
[4] $g\ cm^{-3}$
[5] $mg\ g^{-1}$
[6] $\mu g\ g^{-1}$

Table 4.9 Correlation between mineral magnetic parameters for composite data from all lake cores at Swanswell Pool (575 samples, critical R = 0.0815 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
χ_{lf}	-						
χ_{hf}	0.9986**	-					
χ_{fd}			-				
SIRM	0.8728**	0.8739**		-			
IRM	0.8594**	0.8613**		0.9475**	-		
HIRM	0.4838**	0.486 **	0.1061*	0.685 **	0.5212**	-	
S-ratio					0.175 **	0.179**	-

** denotes significance of 99.9%

* denotes significance of 99%

ii. Relationship between heavy metals in lake sediment cores and surface samples

There is a high level of correlation between the heavy metal concentrations in individual cores and in the composite data set. Table 4.10 shows the correlation matrix of heavy metals from all cores at the Swanswell Pool. Apart from cores M6 and M10, in which Cd and Ni respectively do not correlate with any other heavy metal, the correlation coefficients displayed are high when compared against the critical value of R for the appropriate sample size. With the exception of core M10, the correlation between Ni and Zn is particularly high. Correlations are generally lower in core M10 than in the other 3 cores. When all the lake cores are taken together (Table 4.11), the highest correlation is that between Cu and Pb with an R value of 0.8691.

Fewer significant correlations are found between heavy metals in the top 1 cm of each lake core, as shown in Table 4.12. The highest correlation coefficient is between Cd and Ni with an R value of 0.9053.

Correlations between heavy metals are thus inconsistent, especially in the surface samples. The relationship between Zn and Cd highlighted in the literature (Manahan, 1993) and discussed in Chapter 2.5ii does not appear in correlations from Swanswell Pool.

Table 4.10 Swanswell Pool correlations between heavy metals in individual lake cores

Core M3 (50 samples, critical R = 0.2734 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.7088**	-			
Zn	0.7091**	0.9034**	-		
Pb	0.4117*	0.5081**	0.5204*	-	
Cu	0.7374**	0.8881**	0.935**	0.6739**	-

Core M6 (46 samples, critical R = 0.288 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni		-			
Zn		0.9074**	-		
Pb		0.6698**	0.6415**	-	
Cu		0.7945**	0.7433**	0.8511**	-

Core M8 (34 samples, critical R = 0.3335 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.799**	-			
Zn	0.9287**	0.9144**	-		
Pb	0.5639**	0.773**	0.7331**	-	
Cu	0.7313**	0.8928**	0.8942**	0.9356**	-

Core M10 (47 samples, critical R = 0.2734 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni		-			
Zn	0.7754**		-		
Pb	0.412*		0.4924**	-	
Cu	0.4323*		0.6623**		

Table 4.11 Swanswell Pool correlation between all lake cores with heavy metal analysis.
(177 samples, critical R = 0.1946 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.2978**	-			
Zn	0.3245**		-		
Pb	0.4188**	0.4443**	0.2173*	-	
Cu	0.5657**	0.5236**	0.3768**	0.8691**	-

Table 4.12 Swanswell Pool correlation between heavy metals in surface lake sediment samples.
(12 samples, critical R = 0.6021 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.9053**	-			
Zn	0.7073*	0.6478*	-		
Pb				-	
Cu					-

iii. Correlation and regression between heavy metal concentration and mineral magnetic parameters.

Tables 4.13 and 4.14 give correlation matrices of heavy metals and mineral magnetic parameters for individual lake cores. There is little correlation shown in core M3, except between Ni, χ_{lf}, χ_{hf} and the S-ratio. The correlation coefficient values are low and do not exceed 0.5, although they are still significant at the 99.9% level. There is also little correlation in core M10. Here, the three derived magnetic parameters, χ_{fd}, S-ratio and HIRM correlate with Cd and Cu; Ni and Cu; and Zn respectively, but only the relationship between Ni and the S-ratio exceeds a coefficient of 0.4 and it is the only value significant at the 99.9% level.

The top 1 cm samples of the lake cores exhibit no significant correlation between heavy metals and magnetic parameters.

Regression was also carried out between heavy metals and magnetic parameters on individual cores. This was to determine whether mineral magnetic characteristics could be used to predict the levels of heavy metals in a sample. Cores M6 and M8 were chosen for this analysis as there was little correlation between these parameters in cores M3 or M10. The data were selected on the basis of a correlation coefficient at the 99.9% significance level and high values, such as Cu with χ_{lf} in core M6 (0.7133**, Table 4.13). The scattergrams

Table 4.13 Swanswell Pool correlations between heavy metals and mineral magnetic parameters

All cores with heavy metal analysis: no correlation

Core M3 (50 samples, critical R = 0.275 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd							
Ni	0.481**	0.4993**					0.4473**
Zn							
Pb							
Cu							

Core M6 (46 samples, critical R = 0.2875)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd							
Ni			0.3749*				
Zn	0.4889**	0.4659**	0.4182*				
Pb	0.7547**	0.7324**	0.6118**	0.5035**	0.5211**	0.4645**	
Cu	0.7133**	0.6656**	0.6946**	0.3988*	0.4088*	0.4058*	

Core M8 (34 samples, critical R = 0.335)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.4497*	0.4518*			0.4768*		
Ni	0.7680**	0.7666**		0.6937**	0.7074**	0.4098*	0.4098*
Zn	0.6010**	0.6007**		0.4672*	0.5606**		
Pb	0.7154**	0.7148**	0.4373*	0.5473**			
Cu	0.7173**	0.7157**	0.4018*	0.5041*	0.5777**		

Table 4.13 (continued) Swanswell Pool correlations between heavy metals and mineral magnetic parameters

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Core M10 (47 samples, critical R = 0.2875)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd				0.394*			
Ni							0.473**
Zn						0.3525*	
Pb							
Cu				0.4224*			0.3576*

Top 1 cm lake core samples: no correlation

---

are presented in Figs 4.22 to 4.25 with the associated percentage explained variance and regression equations. In linear regression, the fitted line is described by an equation of the form

$$Y = a + bX$$

Where Y is the dependent variable and X is the independant variable. Y is therefore to be predicted from X. The gradient

Fig 4.22 Core M8 regression
a. Zn with χ_{lf}
b. Pb with χ_{lf}

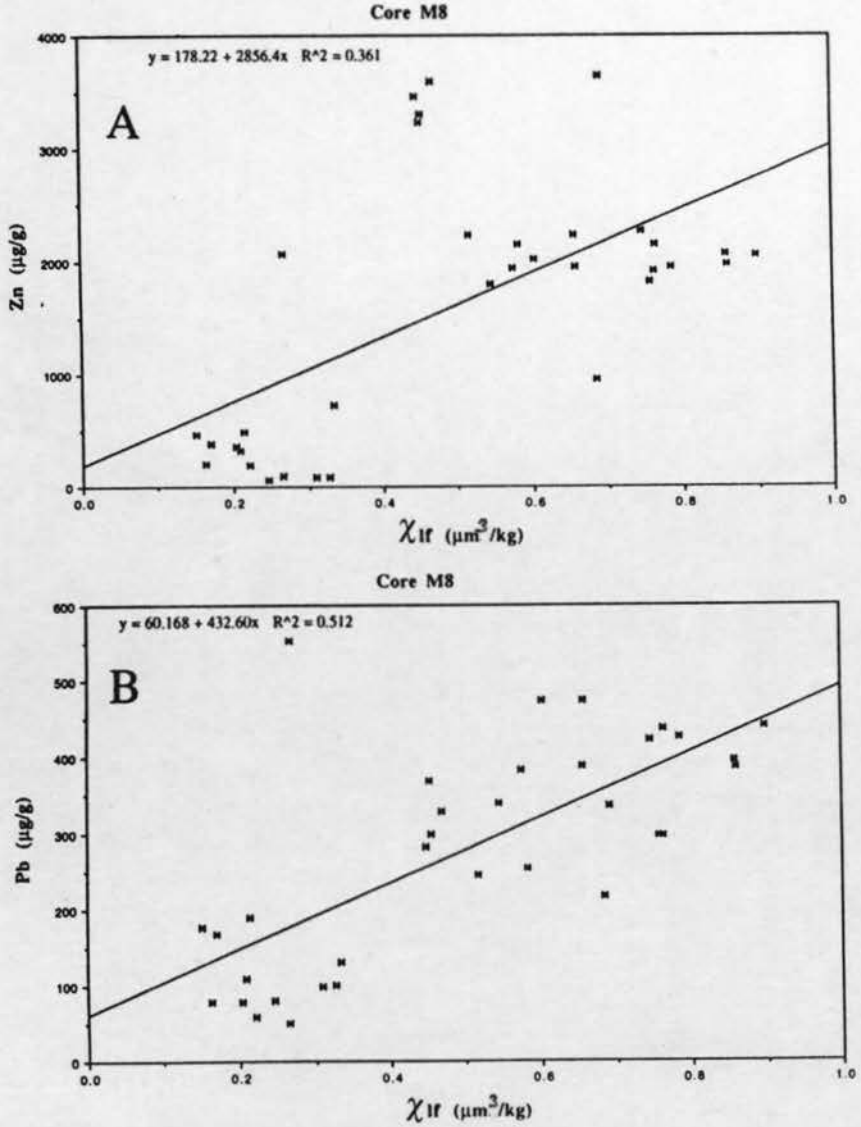


Fig 4.23 Core M8 regression
a. Ni with χ_{lf}
b. Cu with χ_{lf}

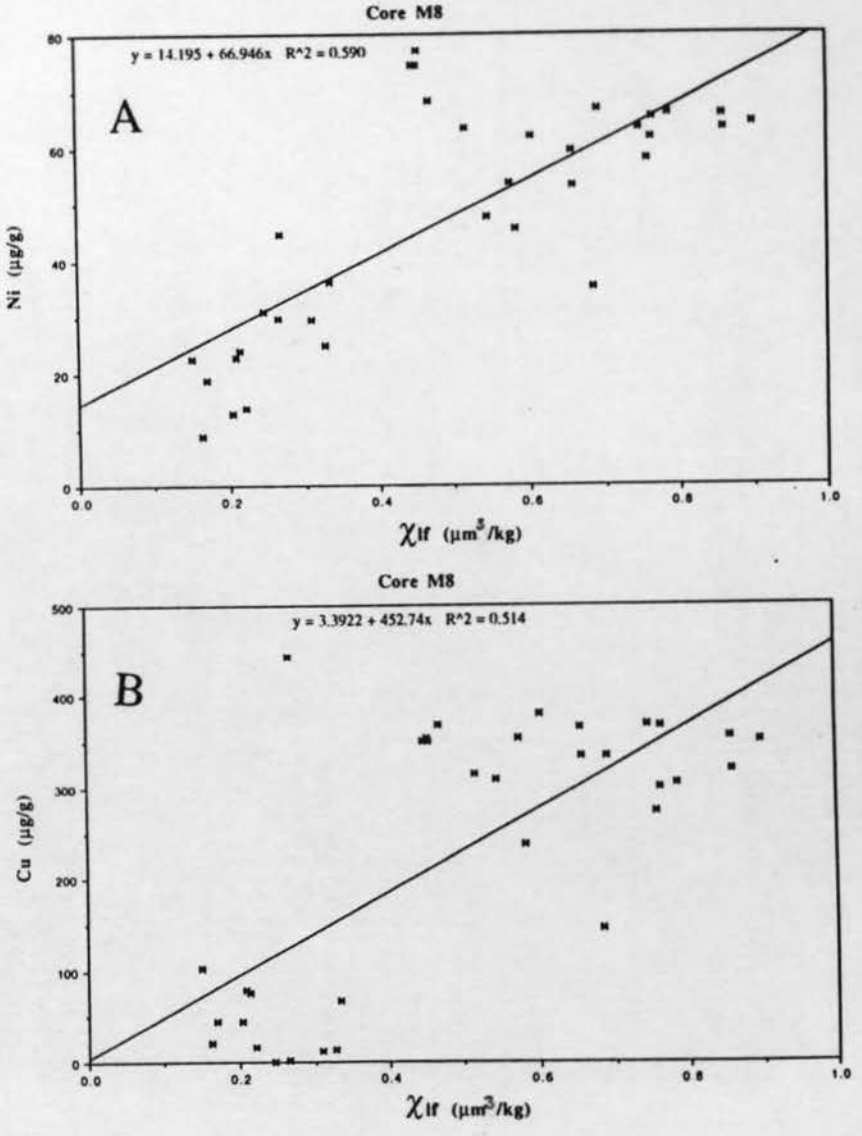


Fig 4.24 Core M8 regression, Ni with SIRM

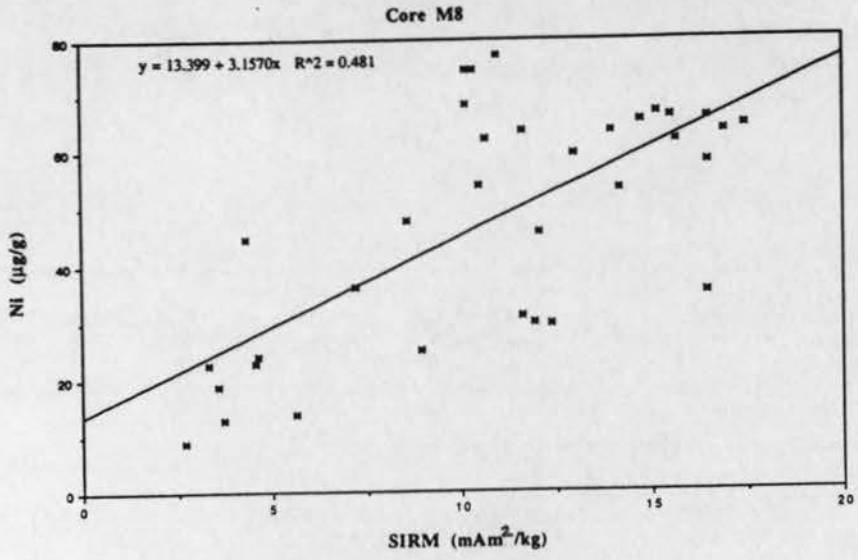
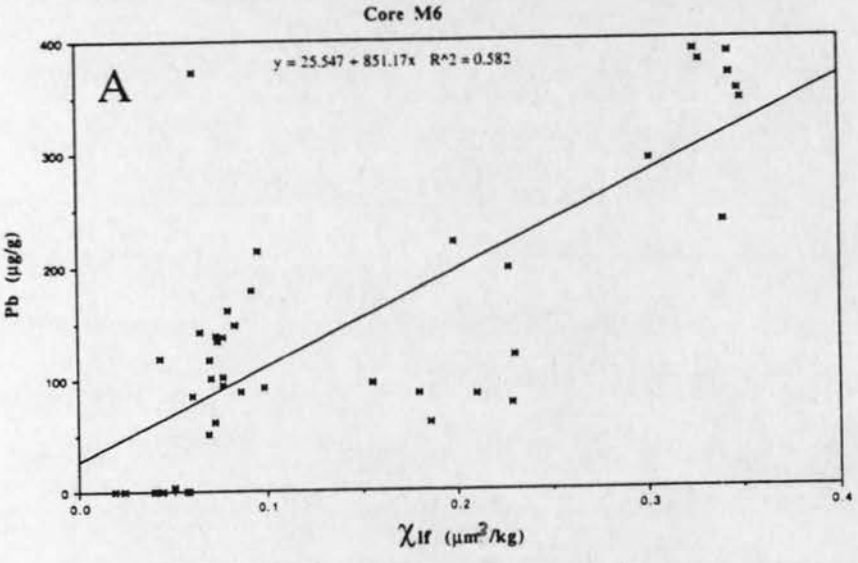
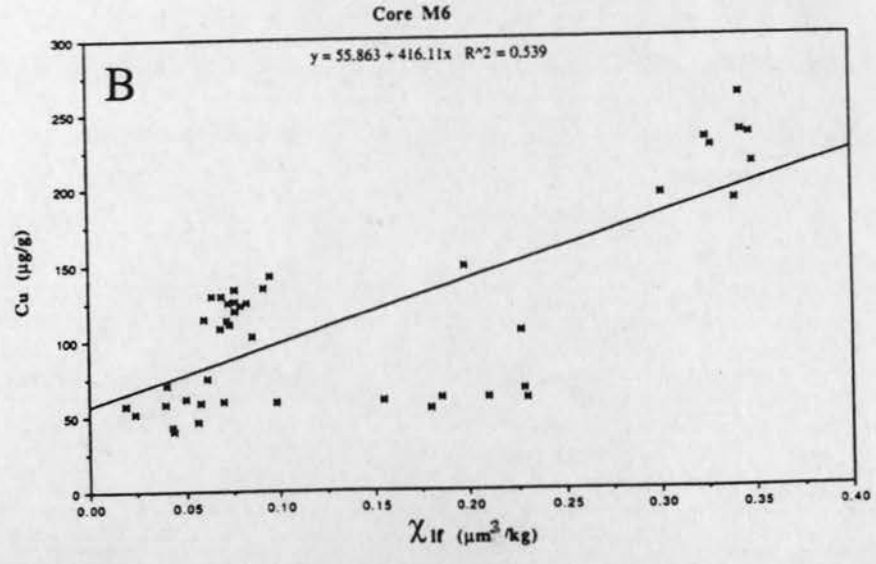


Fig 4.25 Core M6 regression
a. Cu with χ_{lf}
b. Pb with χ_{lf}





of the regression lines are all positive indicating that as the mineral magnetic parameter increases, so does the heavy metal concentration.

The R^2 value quantifies how strong the relationship is between heavy metals and mineral magnetic characteristics. The R^2 value represents the coefficient of determination, this represents the proportion of Y explained by the regression equation. The closer the R^2 value approaches 100%, the more the variation in Y is explained by the regression equation (Gordon *et al.*, 1992). With R^2 values of 33.84% and 38.1% for cores M6 and M8 respectively, the parameters tested which explain the least variance are Zn with χ_{lf}. The majority of the other combinations explain more than 50% of the variance in the data. However, cores M6 and M8 are alone in exhibiting any such relationship, and the results from core M6 indicate significant correlation between Cu and Pb with χ_{lf} only so the relationships demonstrated are not consistent. When consideration of all the cores with heavy metals is made, there is no demonstrable relationship between heavy metals and magnetic parameters in the bulk data set.

The scattergrams indicate two populations of points; those with high values for both the magnetic parameter and heavy metal concentration, and those with low values for both. The low values in each case represent the samples at the base of the core, the higher values are a mixture of the samples from the middle to the top of the core.

v. Relationships between particle size and heavy metal concentration.

As discussed in Chapter 2.8.id, there are many studies which have found an inverse relationship between increasing heavy metal concentration and decreasing particle size (Förstner & Patchineelam, 1980; Förstner & Wittmann, 1981; Horowitz, 1991). Whilst this study did not attempt to partition the heavy metal concentration in the sediment according to particle size, particle size analysis was carried out separately on core M8 for which there was also heavy metals data. The mean particle size (Fig 4.19) varied from between about 10 to 35 μm (fine to medium silt). Table 4.14 shows the correlation matrix between the mean, median and span (the sorting index) of lake sediment particle size from core M8 with heavy metal concentration. There is no correlation between the heavy metals and span, but there is a correlation greater than the 99% significance level between the median and mean particle size and all heavy metals. There is particularly significant correlation (at the 99.9% significance level) between Pb and Cu and both the median and mean particle size. Cd and Ni show the lowest levels of correlation. It has been shown (Tables 2.10 and 2.11) that Pb has the highest K_D and that it is most strongly sorbed to particulate matter. Zn transported in rivers in the English Midlands (Proffitt, 1993) however, is preferentially transported in solution, although its' K_D, according to Sigg (1983) is more than that of either Cu and Cd. Sigg (1983) suggested that 90% of the Cd and Cu would be preferentially transported in solution.

Table 4.14 Correlation between particle size and heavy metals from core M8 (34 samples, critical R = 0.3494 at 99%)

	Cd	Zn	Pb	Ni	Cu
Median	0.4230*	0.5099*	0.74**	0.4902*	0.688**
Mean	0.4353*	0.5271**	0.7458**	0.51*	0.6996**
Span	no correlation with heavy metals				

* denotes significance at 99.9%

** denotes significance at 99%

With increasing solubility, therefore, the correlation between particle size and sediment associated heavy metals appears to get poorer. However, Honeyman & Santschi (1988) state that the K_D for an element is site specific and may reflect many environmental variables (see Table 2.12). The availability, heterogeneity and state (aggregation, dissolution and presence of other substances on the sorption sites) of the particles also affects the rate of removal of metals from solution (Honeyman & Santschi, 1988). Foster *et al.* (1994) have shown that the proportion of soluble heavy metals was affected by the total concentration in solution such that as the total heavy metal concentration increased, the relative amount sorbed to particulates decreased. Direct causality therefore

cannot be inferred since the relationship between particles and sorbed heavy metals is far from being a simple one.

Whilst the complex interactions between particles and heavy metals are beyond the scope of this study, it would provide a suitable subject for further work.

b. Principal Component Analysis (PCA)

PCA reduces the number of variables to a set of dominant factors which enables the associations to be isolated. The first factor accounts for as much of the variation in the original data set as possible. The second factor then accounts for as much of the remaining variance as possible which is not correlated with the first factor. PCA does this by examining the data set, determining interrelationships and creating a new data set from the original, effectively reducing the number of variables. In such a large set of data as has been collected in this study, PCA is therefore a useful statistical tool (Gordon *et al.*, 1992). At Swanswell Pool, it was applied to the lake sediment cores with heavy metals data and included all the other parameters measured such as bulk density and mineral magnetic properties.

Figs 4.26 a - d plot the eigenvalues and Tables 4.15 to 4.17 present the varimax rotated factor matrices from the lake cores. Table 4.18 a lists the percentage contribution to the total variance of the individual factors in the data set. In all the cores the first two factors contributed over 55% to the total variance. The factor matrix plots utilised factors 1 and 2 only (Figs 4.27 a - d).

Factor	Eigenvalue	Pct of Var	Cum Pct
1	7.46345	39.3	39.3
2	5.89325	31.0	70.3
3	1.45943	7.7	78.0
4	1.22277	6.4	84.4
5	.76685	4.0	88.5
6	.69699	3.7	92.1
7	.53060	2.8	94.9
8	.31421	1.7	96.6
9	.24500	1.3	97.9
10	.17918	.9	98.8
11	.10300	.5	99.3
12	.06962	.4	99.7
13	.02340	.1	99.8
14	.01864	.1	99.9
15	.00825	.0	100.0
16	.00321	.0	100.0
17	.00207	.0	100.0
18	.00008	.0	100.0
19	.00000	.0	100.0

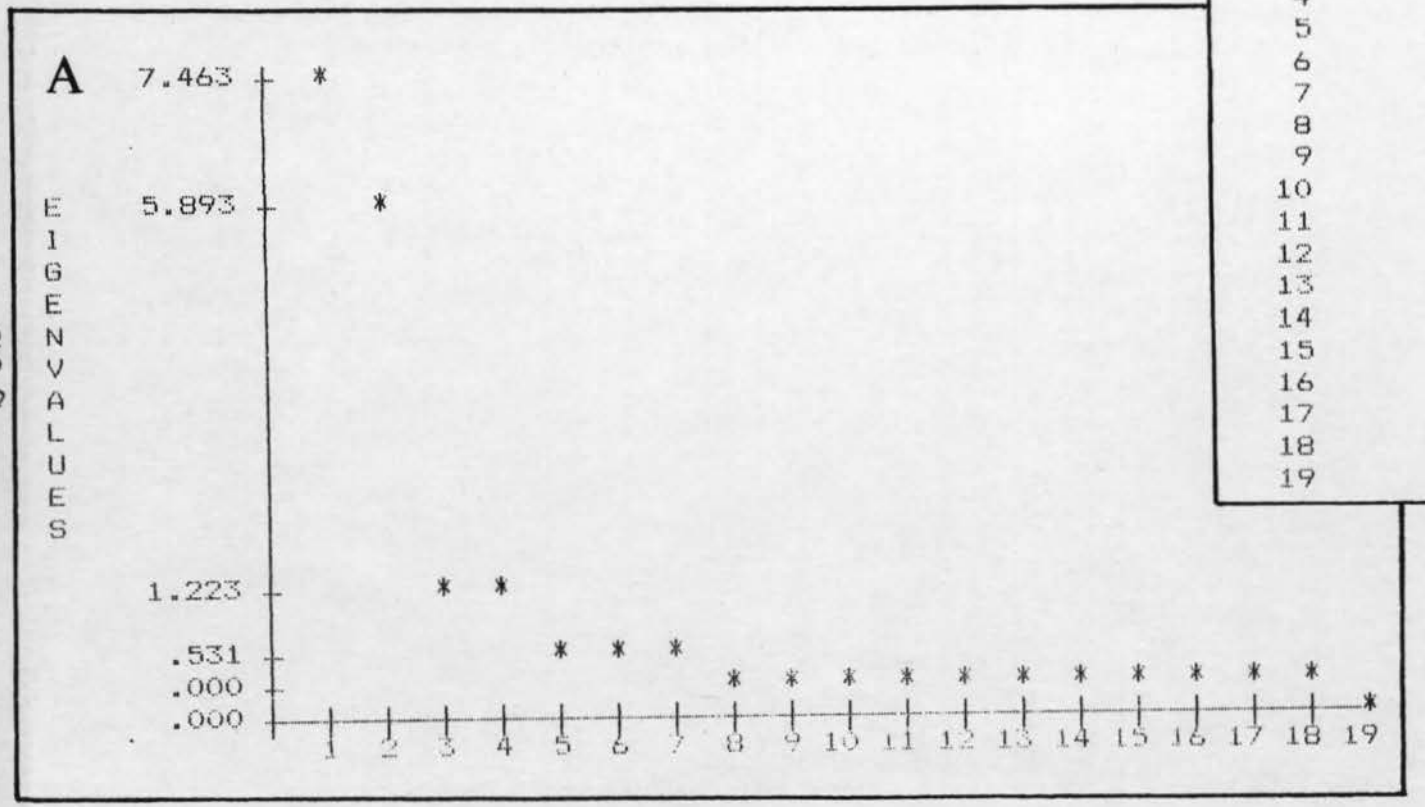
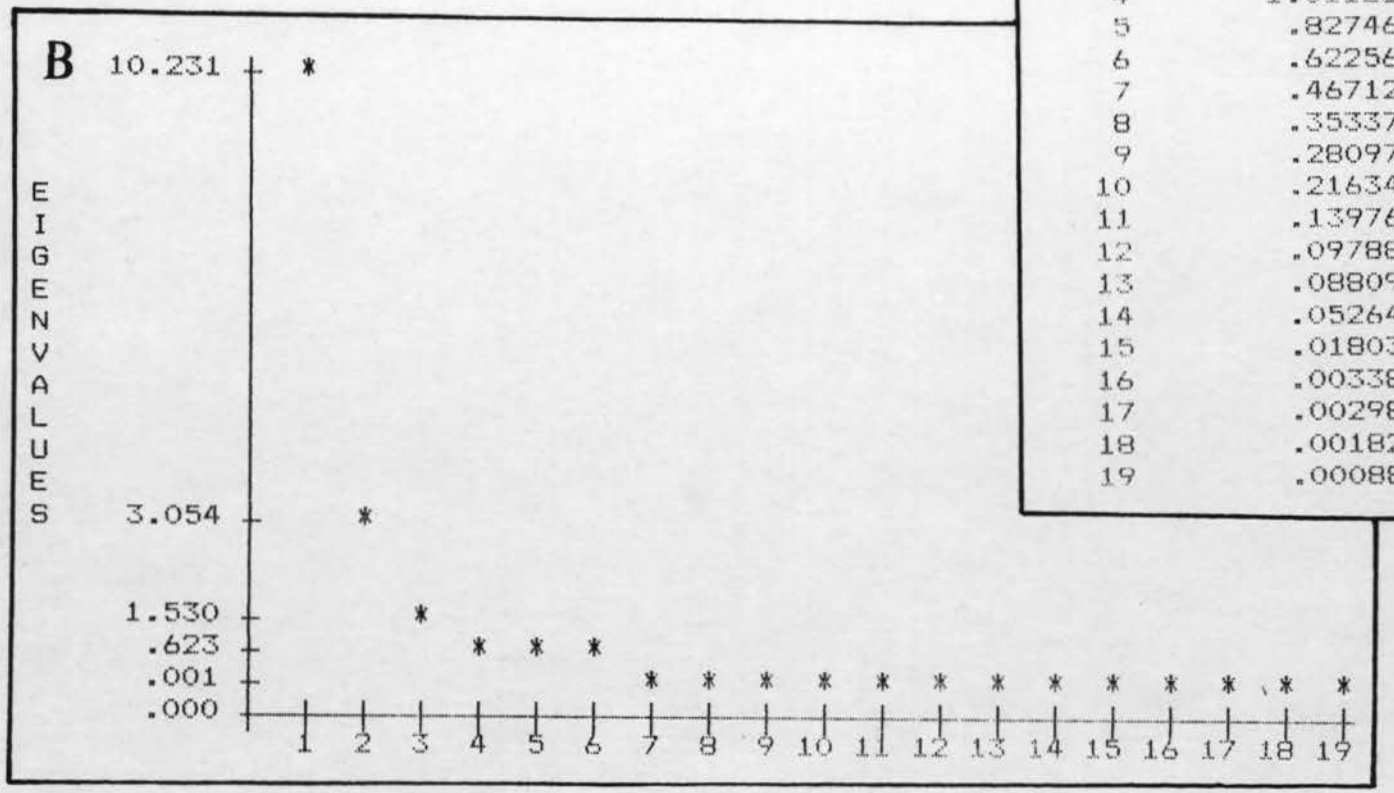
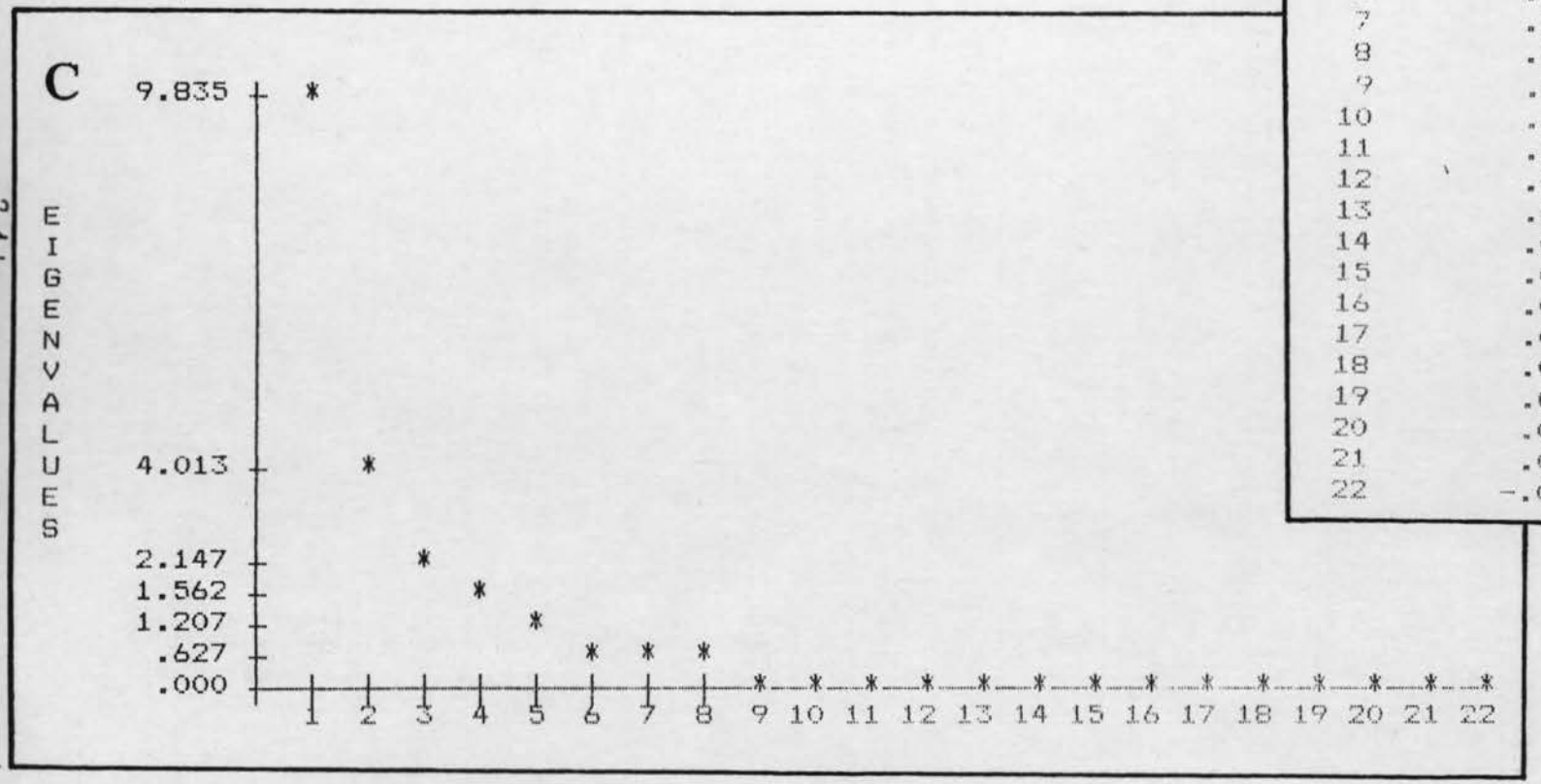


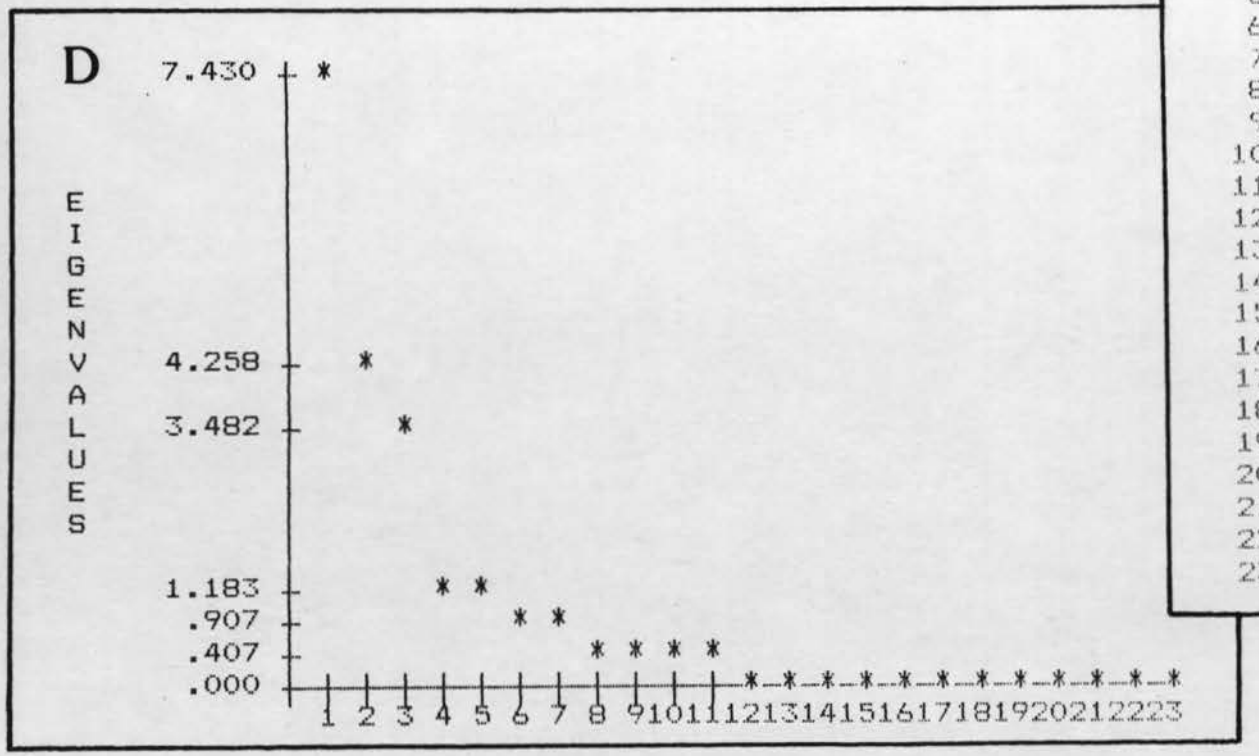
Fig 4.26 Eigenvalues
a. core M3
b. core M6
c. core M8
d. core M10



Factor	Eigenvalue	Pct of Var	Cum Pct
1	10.23116	53.8	53.8
2	3.05432	16.1	69.9
3	1.53001	8.1	78.0
4	1.01123	5.3	83.3
5	.82746	4.4	87.7
6	.62256	3.3	90.9
7	.46712	2.5	93.4
8	.35337	1.9	95.2
9	.28097	1.5	96.7
10	.21634	1.1	97.9
11	.13976	.7	98.6
12	.09788	.5	99.1
13	.08809	.5	99.6
14	.05264	.3	99.9
15	.01803	.1	100.0
16	.00338	.0	100.0
17	.00298	.0	100.0
18	.00182	.0	100.0
19	.00088	.0	100.0

Factor	Eigenvalue	Pct of Var	Cum Pct
1	9.83512	44.7	44.7
2	4.01297	18.2	62.9
3	2.14740	9.8	72.7
4	1.56224	7.1	79.8
5	1.20685	5.5	85.3
6	.89168	4.1	89.3
7	.75791	3.4	92.8
8	.62672	2.8	95.6
9	.40150	1.8	97.5
10	.25167	1.1	98.6
11	.14111	.6	99.3
12	.07131	.3	99.6
13	.03954	.2	99.8
14	.01833	.1	99.8
15	.01618	.1	99.9
16	.00809	.0	99.9
17	.00589	.0	100.0
18	.00291	.0	100.0
19	.00150	.0	100.0
20	.00103	.0	100.0
21	.00006	.0	100.0
22	-.00000	-.0	100.0





Factor	Eigenvalue	Pct of Var	Cum Pct
1	7.43033	32.3	32.3
2	4.25829	18.5	50.8
3	3.48231	15.1	66.0
4	1.49988	6.5	72.5
5	1.18292	5.1	77.6
6	1.03569	4.5	82.1
7	.90692	3.9	86.1
8	.64897	2.8	88.9
9	.55088	2.4	91.3
10	.47586	2.1	93.4
11	.40682	1.8	95.1
12	.33796	1.5	96.6
13	.19433	.8	97.4
14	.17025	.7	98.2
15	.12668	.6	98.7
16	.10858	.5	99.2
17	.08149	.4	99.6
18	.05588	.2	99.8
19	.02598	.1	99.9
20	.01702	.1	100.0
21	.00297	.0	100.0
22	.00001	.0	100.0
23	-.00000	-.0	100.0

Table 4.15 Varimax rotated factor matrix (n = 19, critical R = 0.5721 at 99%)

a. core M3

b. core M6

Rotated Factor Matrix:

A

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
LFX	.67346	.19623	.63604	.22388
HFX	.67135	.21785	.63989	.18677
SIRM	.91434	-.13339	.30015	.12017
IRM	.80008	-.08809	.47746	.23499
FDX	.05146	-.00784	.12547	.85445
S_RATIO	-.89276	-.21339	.19408	.14556
HIRM	.92927	-.15702	.14417	.02491
DBD	.12966	-.82034	-.18296	.45068
WBD	.01877	-.32581	-.19410	.58711
DWR	.12010	-.86643	-.19995	.22921
CD	-.05626	.73725	-.12973	-.28630
ZN	-.02277	.93557	.13675	.00698
PB	-.03008	.72922	-.43571	.08937
NI	.32066	.90155	.15360	.01927
CU	-.01596	.98131	.00268	-.04929
FE	.91447	.07494	.24435	-.10269
MN	.97477	.02266	.01206	.04093
FE_MN	.34884	.19006	.64948	-.32973
P	.38735	.69403	.24472	.08603

B

LFX	.54356	.80365	-.03525	.15453
HFX	.47787	.84009	-.02858	.06931
SIRM	.14209	.95840	.12289	.08689
IRM	.20405	.95558	-.08109	.07220
FDX	.65797	.32087	-.05210	.39351
S_RATIO	-.01659	.04071	-.71298	-.01332
HIRM	.12809	.87485	.20852	.13677
DBD	-.95382	-.11994	.04713	-.03701
WBD	-.82159	-.19691	.21812	-.00665
DWR	-.96184	-.14326	-.05002	-.08423
CD	.08128	-.15036	.00258	-.85578
ZN	.79917	.12903	.25836	-.23469
PB	.75510	.41860	.14589	.04951
NI	.77018	.12582	.40902	-.24692
CU	.89389	.27536	.24013	.05817
FE	.22448	.65451	.61170	.17743
MN	.18948	.59618	.65312	-.02559
FE_MN	.34444	.54610	.27788	.50295
P	.77358	.36684	.13864	.13083

Rotated Factor Matrix:

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
LFX	.41776	.88167	.15866	.07706	-.06102
HFX	.41341	.88148	.16141	.08074	-.06924
SIRM	.09727	.91492	.18426	.32738	-.02557
IRM	.16434	.93558	.26714	.00886	.05486
FDX	.53749	.23558	-.17701	-.04895	.39254
S_RATIO	.24350	.17937	.22828	-.86293	.22142
HIRM	-.06354	.53555	-.03830	.79679	-.16538
DBD	-.81045	-.13752	.11029	-.22837	-.12228
WBD	-.95620	-.21067	.00650	.07146	.02033
DWR	-.94411	-.17184	-.00677	.10517	.03510
CD	.30178	.22104	.84015	-.01830	.00651
ZN	.50533	.30596	.73781	.06724	-.00663
PB	.82812	.34944	.31345	.07869	.00880
NI	.49843	.50534	.59890	.26190	.00354
CU	.77884	.34729	.47974	.09487	.00569
FE	.18193	.35125	.30840	.77659	.27973
MN	-.03290	.29058	.59276	.67718	.17223
FE_MN	.30900	-.08227	-.68734	.03127	.16537
P	.39489	.05921	-.15850	-.05673	.51138
MEDIAN__	.72330	.06446	.36735	-.28663	.18399
MEAN	.72814	.11759	.36879	-.28599	-.01941
SPAN	.12170	.15988	.04857	.00011	-.83876

Table 4.16 Varimax rotated factor matrix (n = 22, critical R = 0.4921 at 99%), core M8

Rotated Factor Matrix:

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6
LFX	-.04762	.33815	.83695	.01146	.16900	.28214
HFX	-.05514	.33727	.84000	.01294	.16379	.27556
SIRM	.04744	-.12005	.68551	-.08984	-.01231	.68386
IRM	-.00045	.10946	.56585	-.14335	-.00571	.77448
FDX	.11659	.22109	-.00881	-.11597	.57748	.38099
S_RATIO	-.20040	.70328	.04664	-.29118	.05254	.52789
HIRM	.14736	-.65790	.62394	.10026	-.02292	.07000
DBD	.93093	-.13328	-.01840	.05396	.02939	.03499
WBD	.88053	.04439	.04562	.10017	.02351	.07969
DWR	.91289	-.27138	.01512	.02786	-.14680	-.00545
CD	-.75149	.31273	.04540	.11325	.14594	.16673
ZN	-.76924	.28796	-.10730	-.02187	.35490	.03765
PB	.43742	.03827	.00113	-.26153	-.28865	-.39347
NI	.16110	-.23286	-.10329	.85470	-.04348	-.02023
CU	-.35046	.25439	-.05509	-.17925	.81443	-.00862
FE	.16963	-.55681	-.07678	.75277	-.01707	-.11996
MN	.23971	-.78178	-.10604	.22896	-.10948	-.11319
FE_MN	-.25567	-.21784	.12655	.87208	.00763	-.05773
NA	-.12865	.79184	.13335	-.19007	-.03879	-.06616
K	.14378	-.75349	-.14006	.45805	-.09920	-.05676
CA	.28255	.34249	-.13931	-.29138	-.72481	.17444
MG	-.28057	.66747	.45939	-.08377	.19118	-.03317
P	.11501	.00261	.78960	-.03490	.20936	-.11037

Table 4.17 Varimax rotated factor matrix (n = 23, critical R = 0.535 at 99%), core M10

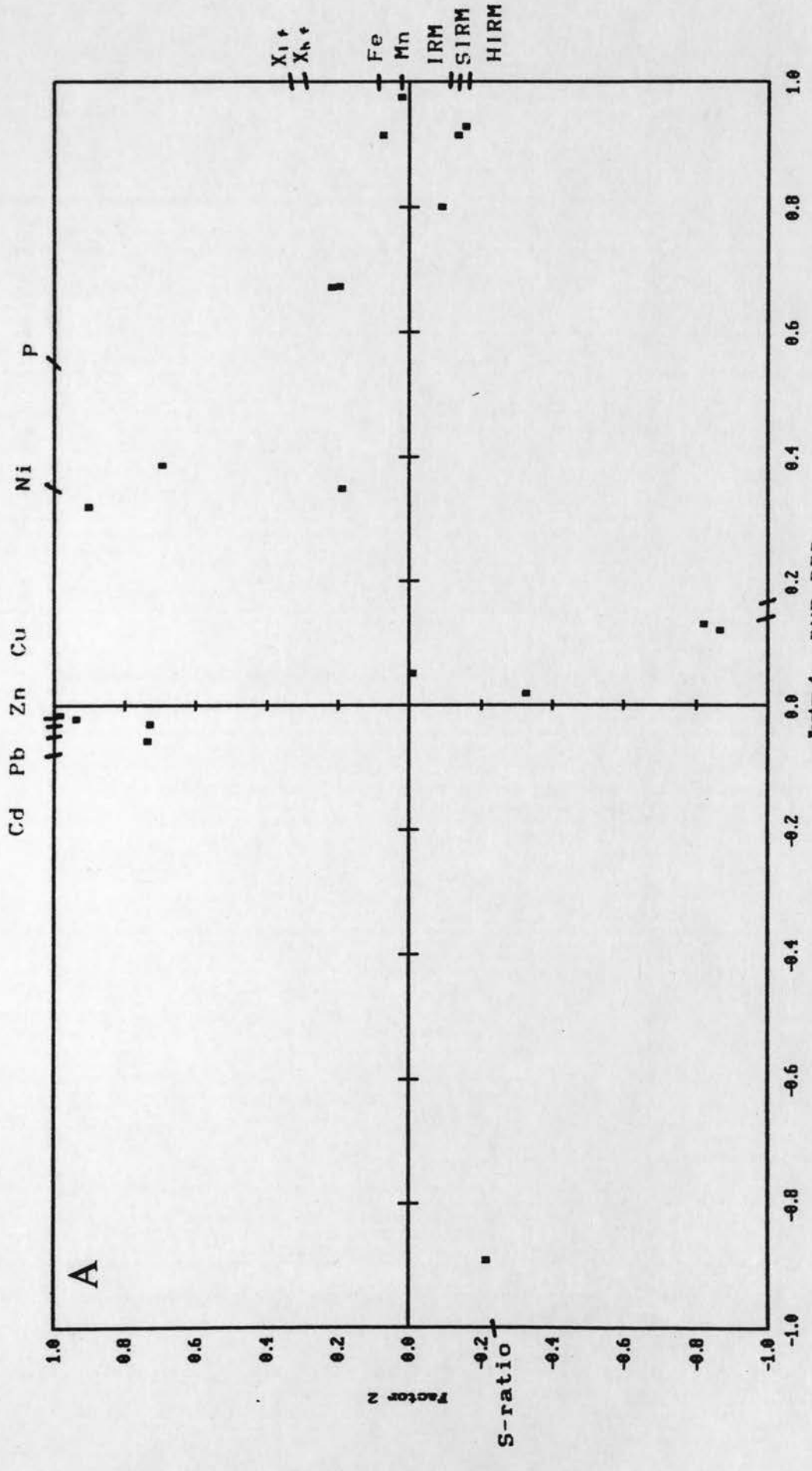
Table 4.18 a Percentage variance of Principal Components in Swanswell Pool lake cores

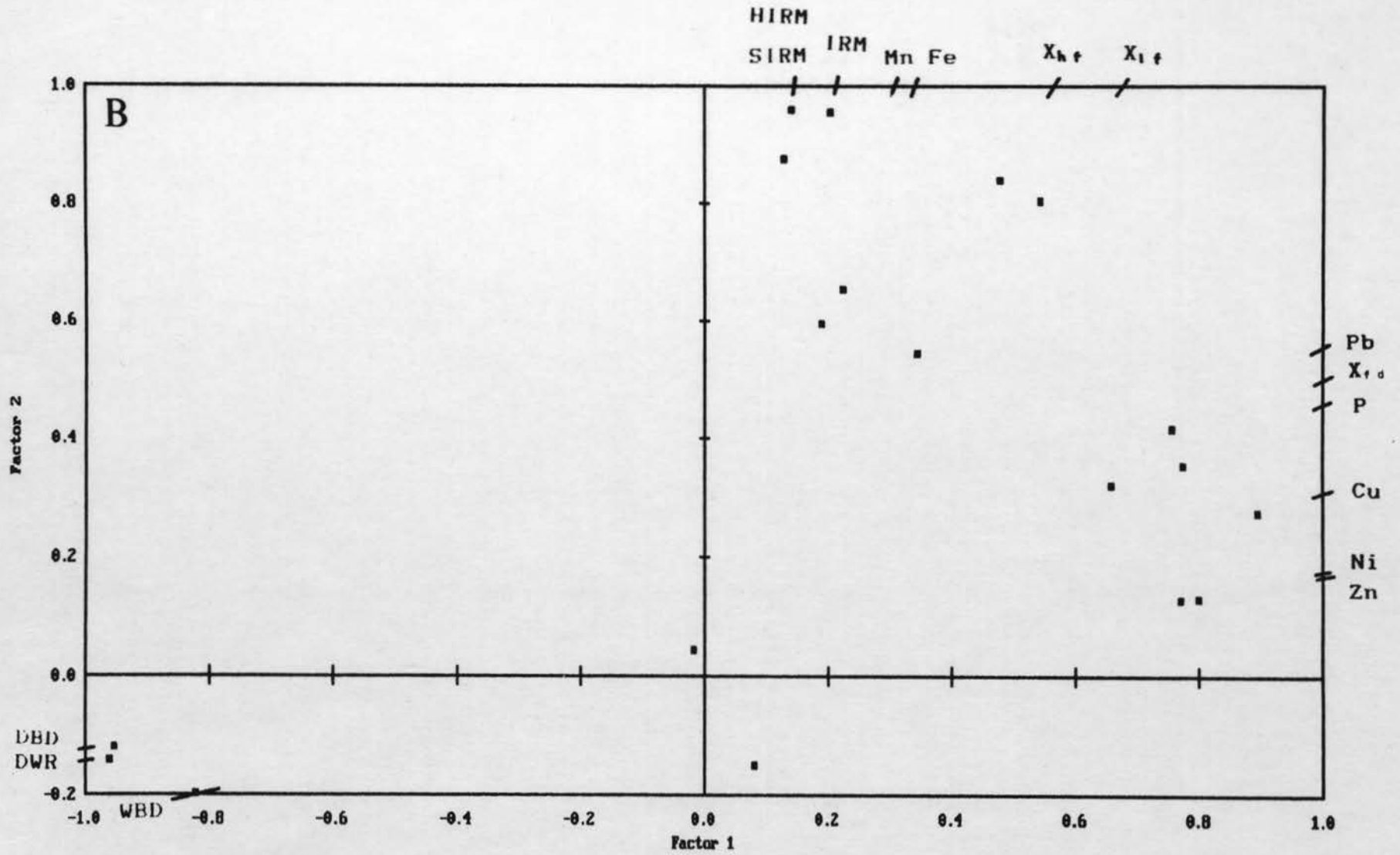
	Factor				
Core	1	2	3	4	5
M3	39.279	31.016	6.437		
M6	53.847	16.074	8.052	3.279	
M8	44.705	18.241	9.759	7.1	5.486
M10	35.381	20.276	16.581	5.633	4.319

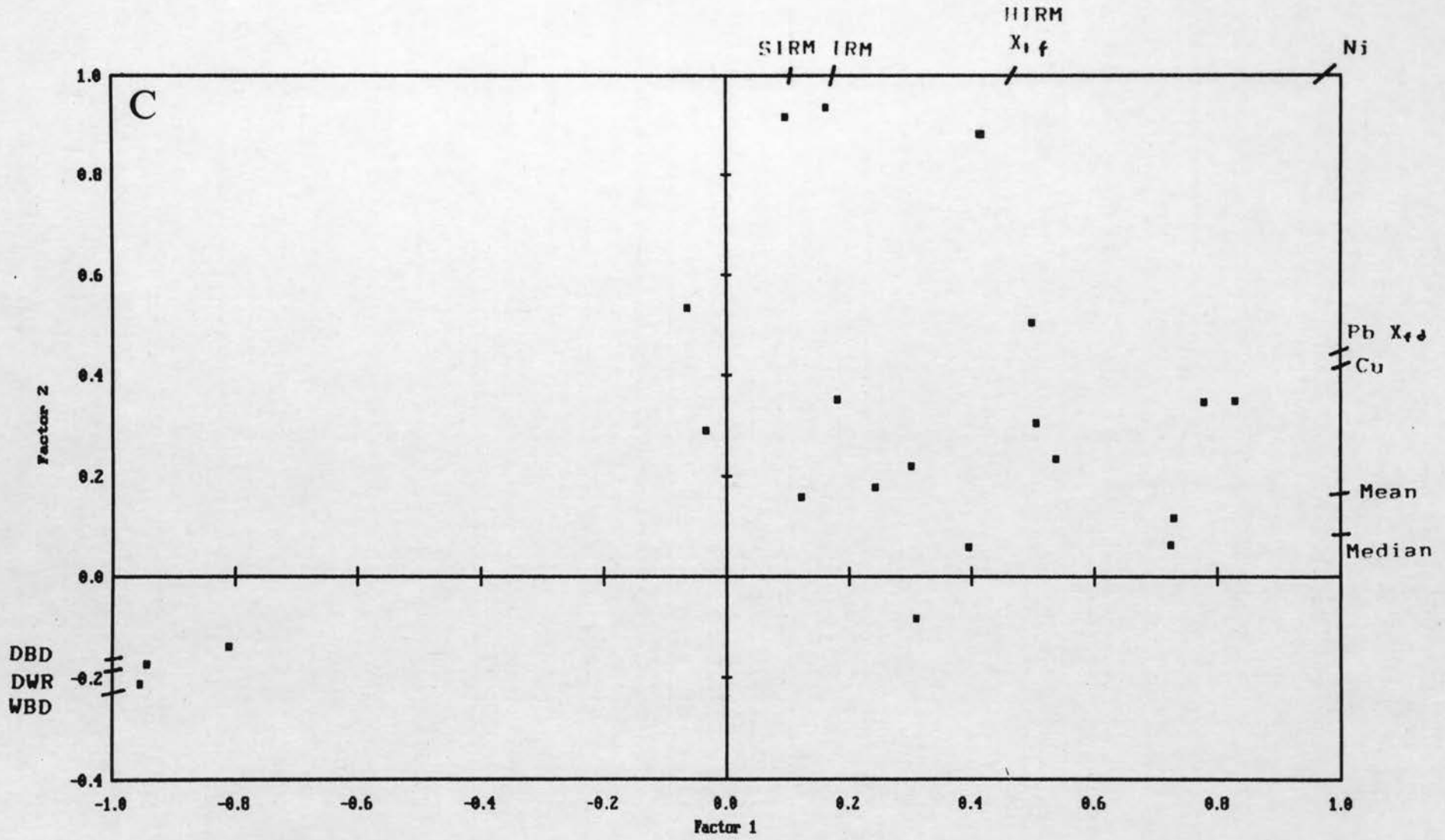
Table 4.18 b lists the parameters which dominate the factors. Some of the heavy metals and all the bulk density parameters feature in factor 1 in all the cores except M3, which is dominated by the measured magnetic parameters, HIRM, Fe and Mn.

Apart from core M3 where factor 2 features mainly heavy metals and some bulk density characteristics, mineral magnetic parameters and Fe and Mn feature strongly in the remaining three cores. X-Y plots of the 2 dominant factors (Figs 4.27 a - d) indicate the strength of the relationship between the variables in the 2 dominant factors. Only the variables with the highest level of component loading (those above the critical value indicated on Tables 4.11 to 4.13) are indicated on these plots; unlabelled points represent those variables with the weakest loading.

Fig 4.27 Rotated factor plot
a. core M3
b. core M6
c. core M8
d. core M10




B
HIRM
SIRM
IRM
Mn
Fe
X_{hf}
X_{lf}
Pb
X_{fd}
P
Cu
Ni
Zn
DBD
DWR
WBD
Factor 1
Factor 2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0


C
HIRM
SIRM IRM
X_{lf}
Ni
Pb X_{fd}
Cu
Mean
Median
DBD
DWR
WBD
Factor 2
Factor 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0

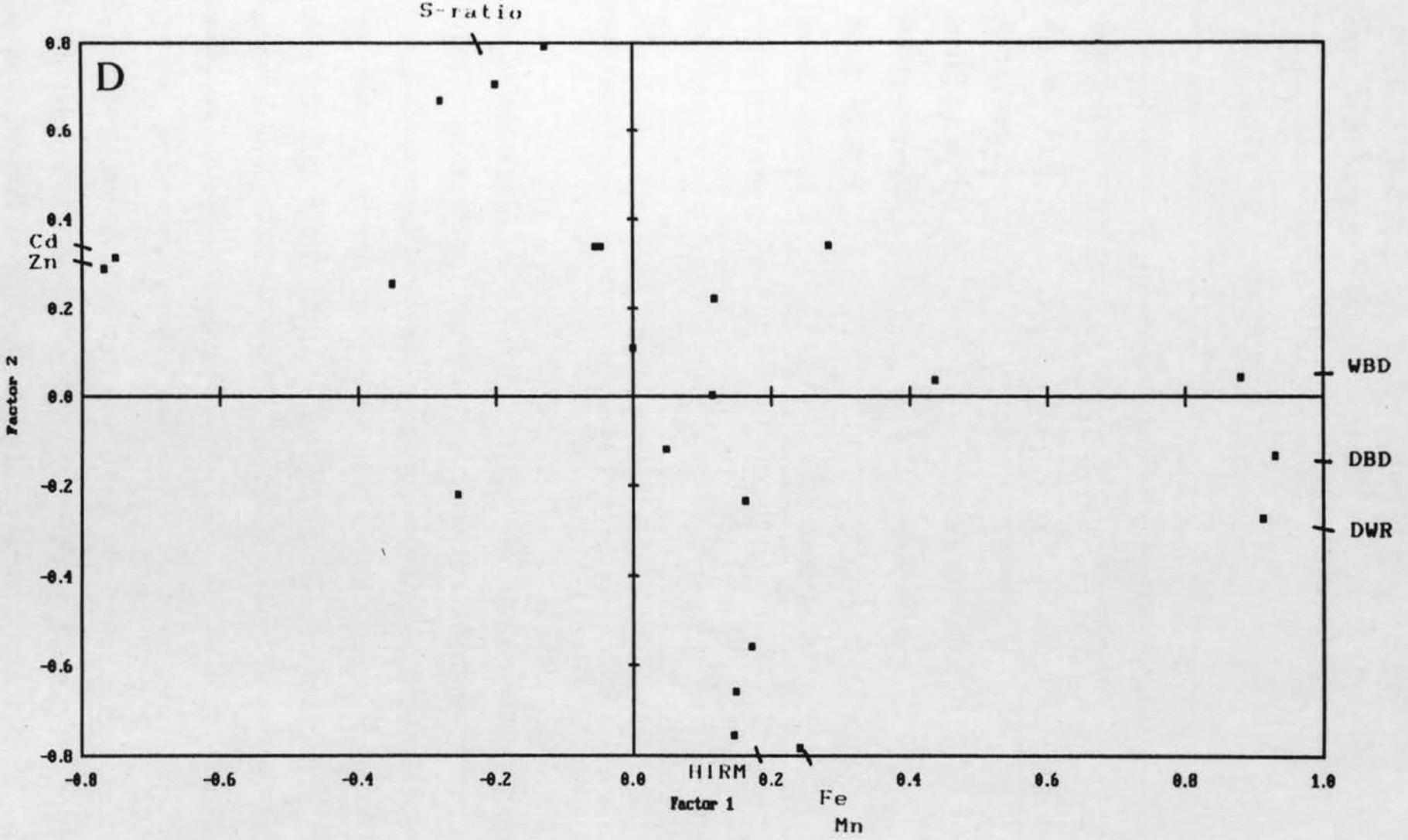

D
S-ratio
Cd
Zn
WBD
DBD
DWR
HIRM
Fe
Mn
Factor 1
Factor 2
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0

Table 4.18 b Dominant parameters identified by Principal Component Analysis in factors 1 and 2

	Factor	
Core	1	2
M3	Magnetics	Heavy metals
	Fe and Mn	P
M6	Heavy metals	Magnetics
	bulk density	Fe and Mn
M8	Heavy metals	Magnetics
	bulk density	
M10	Heavy metals	Magnetics
	bulk density	

4.4 Mollusca.

The molluscan fauna of Swanswell Pool have been discussed in detail by Foster *et al.* (1988). The Mollusca diagram (Fig 4.28) indicates that conditions clearly worsened for Mollusca towards the top of the core. There is a progressive decline in suitable habitat which may reflect decreasing water flow through the pool, which allowed the development of a weed obligate, still water community. This occurs above a depth of 26 - 30 cm, at the boundary between the red clay and the black, organic gyttja and may represent the conditions prevalent when Swanswell Pool was isolated from its inflowing stream as outlined in Chapter 3. The substrate was then

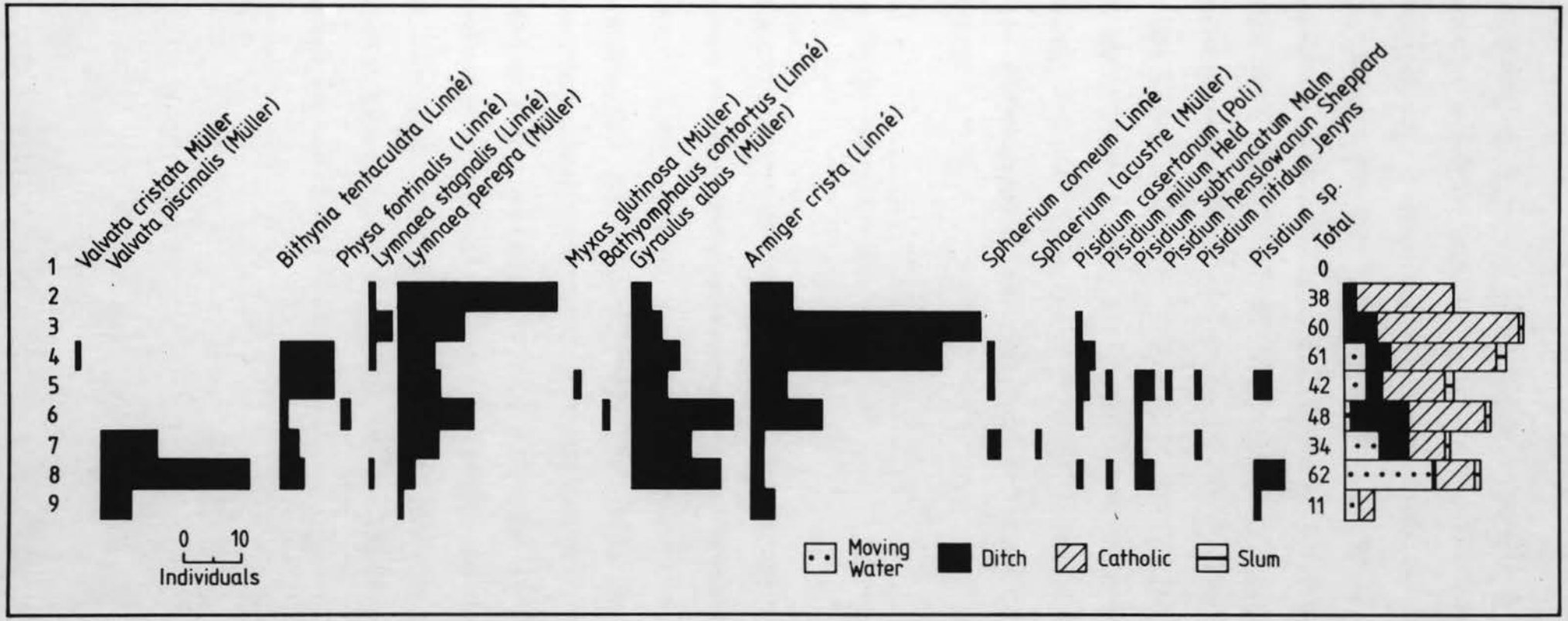


Fig 4.28 Mollusc diagram from Swanswell Pool

disturbed to such a degree above a depth of 11 - 16 cm in the sediment column, that virtually all molluscan species disappeared. It was suggested in Foster *et al.* (1988), that the disturbance may date back to the 1920's and 30's when Swanswell Pool was used for boating. Species diversity and individual numbers of Molluca decline in the upper two samples, where they are dominated by Sparks' (1961) "catholic" group; those that are tolerant of a wide range of substrate and oxygenation conditions. However, Swanswell Pool does support a limited fauna at present as well grown individuals of *L. Peregra* were found on weed removed from the Pool during coring.

4.5 Water quality analysis

This section is divided into three subsections, the first two detail primary data collected during February and April 1988 when in situ analyses and water chemistry in the laboratory were carried out respectively. The third subsection discusses secondary water quality data obtained from the NRA (Severn Trent Region). These data were obtained to determine prevailing environmental conditions to assess whether there was any likelihood of heavy metals bound to sediment particles being released into the water column and thus becoming a hazard to the ecosystem.

4.5.1. In situ analysis

Summary data for water quality characteristics of the Swanswell Pool are presented in Table 4.19. The measurements were taken from a boat in February, 1988, at three depths in the water column, at the point marked S1 on Fig 2.10 a.

Table 4.19 Water quality characteristics of Swanswell Pool in the field at a single site at three depths in the water column

Site	Depth m	pH	O mg l^{-1}	O % sat	Temp °C	Eh mv
S1	0	8.7	13.2	100	3.8	109
S1	0.5	8.7	13.1	99.2	3.8	115
S1	0.75	8.6	12.7	96.2	3.8	76

Location of S1 on Fig 2.10 a
Based on a survey undertaken in February, 1988.

The water sample was highly alkaline, with an average pH of 8.7. Dissolved oxygen levels reduced from 100% saturation at the surface down to 96.2% at the mud-water interface. Lowered dissolved oxygen at the mud-water interface probably reflects water trapped in benthic weed giving rise to partially deoxygenated conditions. There was no variation in temperature, which remained at 3.8° C from the surface downwards. Eh, the measure of redox potential, decreases with

depth, reaching +76 mv at the mud-water interface. The Eh of the intermediate sample was slightly higher than the one at the surface.

4.5.2. Chemical analysis of water samples

A second water quality survey was undertaken in April 1988. In this case three samples were taken from sites marked on Fig 2.10 a and analysed in the laboratory. The results are presented in Table 4.20. The most likely source of pollution in the future at Swanswell Pool is the hospital overflow, and although the NRA (Severn Trent Region) stated that leakage was unlikely (J. Batty, pers comm), this was sampled as were the mains water which supplies the Pool and the lake water itself.

The pH of the lake water at Swanswell Pool was 7.4, in marked contrast to the readings obtained during the February 1988 survey, when the pH was found to be 8.7, possibly illustrating the changing environmental regime at this site or the difference between the field and the laboratory-based meters, since the samples were returned to the laboratory for analysis using a bench pH meter rather than the field probe used in the first investigation.

Conductance was highest in the sample taken from the public water supply with that from the main body of the lake intermediary between this and the sample taken from near the hospital overflow. The sample taken from the public mains was highest in Ca, Mg, NO_3, SO_4, HCO_3 and Si and lowest in Na, K, NH_4, NO_2, Cl and PO_4. The sample near the hospital inflow was highest in Na, K, NH_4, NO_2 and PO_4, and lowest in Ca, Mg, SO_4

Table 4.20 Chemical analysis of water samples from Swanswell Pool.

Sample[a]	S1	S2	S3
pH	7.4	7.3	7.2
Conductance[b]	520.0	459.0	744.0
Ca[c]	36.3	28.8	54.4
Mg[c]	8.9	6.4	16.3
Na[c]	25.5	28.2	21.6
K[c]	3.3	4.0	3.3
NH_4[c]	0.0	0.08	0.0
NO_3[c]	1.1	3.1	5.5
NO_2[c]	0.0	0.08	0.0
SO_4[c]	36.0	53.0	57.0
HCO_3[c]	130.6	109.8	214.2
Cl[c]	44.7	42.2	36.9
PO_4[c]	0.03	0.5	0.01
Si[c]	0.61	2.3	3.55

[a] Location of sampling points also shown on Figure 2.9 a

S1 Swanswell Pool

S2 Hospital drain overflow

S3 Public water supply

[b] $\mu s\ cm^{-1}$

[c] $mg\ l^{-1}$

Analysis based on one sample from each location taken on 7 April 1988.

and HCO_3. The sample from the lake water was highest in Cl and lowest in NH_4, NO_3 and Si. These analyses suggest that the sample taken from the hospital inflow still contains high levels of NO_3 and NO_2 in comparison with the public water supply and the Swanswell Pool.

4.5.3. NRA (Severn Trent Region) records of water quality.

The data available from the NRA (Severn Trent Region) relevant to Swanswell Pool consists of a single sampling point located at the surface water sewer taking outflow from the nearby hospital. These data are summarised in Table 4.21. The water quality at this point is highly variable with periodically high BOD and ammoniacal nitrogen. There is also a history of periodical spillages to this site (J. Batty, NRA (Severn Trent Region), pers comm).

The BOD measurements are not directly comparable with the oxygen concentration given in Table 4.19, but NH_4-N, Cl, pH and NO_3-N are. Ranges for pH given by the NRA (Severn Trent Region) fluctuate around neutral for the nine samples taken. The maximum value for NH_4-N of 3.7 mg l^{-1} indicates the magnitude of the spillages occuring from the settling tank, especially in comparison with the value obtained from the samples taken in April 1988 of 0.08 mg l^{-1}. The value given by NRA (Severn Trent Region) for Cl with a mean of 53.0 mg l^{-1} is slightly higher than those taken in April 1988, but they fall within the range of values given by the NRA (Severn Trent Region). Suspended solids were not measured in the 1988

samples but those given by NRA (Severn Trent Region) vary from 177.0 to 21.0 mg l^{-1} with a mean of 67.9 mg l^{-1}.

Table 4.21 Summary water quality statistics from NRA (Severn Trent Region) of a surface water sewer Swanswell recreation ground (1985-1987).

parameter	pH	Suspended solids	BOD+ATU 5 day	Ammoniacal nitrogen	Nitrogen total oxidised	Chloride
		mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
maximum	7.6	177.0	54.0	3.7	5.5	83.0
minimum	6.8	21.0	8.2	0.02	<0.2	33.0
mean	7.3	67.9	30.1	0.7	2.9	53.0
sample size	9	9	9	9	9	9

Tables 4.22 and 4.23 summarise average water quality data from the NRA (Severn Trent Region) and Bottrill (1994) for rivers in Warwickshire and Prescribed Concentrations or Values (PCVs) for potable water. The water in Swanswell Pool does not exceed any of the PCVs for potable water for the analyses undertaken. In comparison with the study undertaken by

Table 4.22 Average NRA (Severn Trent Region) water quality data from various rivers in Warwickshire and potable water Prescribed Concentrations or Values (PCVs)

	Cl mg l^{-1}	TC* $\mu S\ cm^{-1}$	DO mg l^{-1}	T °C	pH	Class**
1	63.7	854.7	10.27	11.4	7.92	2
n=	16	16	25	25	16	
2	266.0	1269.7	10.87	10.3	7.8	2
n=	26	26	25	25	26	
3	151.7	1053.0	10.3	11.0	7.4	3
n=	25	25	25	25	25	
4	45.0	581.7	11.4	9.4	7.8	1B
n=	10	10	10	10	10	
5	56.0	882.7	10.4	9.87	7.9	2
n=	23	23	23	23	23	
6	400.0	1500.0 at 20° C	5.0	>25.0	5.5-9.5	-

1 = River Avon at Tewkesbury (grid ref SO 893 332)
2 = River Sowe at Baginton (grid ref SP 338 752)
3 = River Sowe at Stoneleigh (grid ref SP 332 728)
4 = Finham Brook at Finham Bridge (grid ref SP 331 740)
5 = River Leam at Leamington (grid ref SP 308 654)
6 = PCV water quality standards

* TC refers to total conductivity

** Class refers to the chemical classification of river water quality where class 4 refers to a river which is grossly polluted and class 1 are rivers of high water quality.

n= number of samples

From Severn Trent Water Authority, 1988/1989 (1 - 5) and 1994 (6).

Table 4.23 Average water quality data from rivers in Warwickshire (Bottrill, 1994) and Prescribed Concentration or Value (PCV)

	Arable n=5	Pasture n=10	Forest n=8	Urban n=8	PCV
Na	43.5	17.62	15.8	29.5	150.0
K	11.57	5.97	5.56	5.89	12.0
Ca	51.4	40.5	39.0	35.5	250.0
Mg	45.4	32.3	24.6	18.8	50.0
CO_3	32.6	18.96	6.9	5.7	NS
HCO_3	250.2	240.0	190.6	204.3	NS
PO_4	0.47	0.18	0.1	0.12	2.2
NH_4	0.16	2.82	0.25	5.38	0.5
NO_3	1.1	1.05	1.5	0.46	50.0
NO_2	0.05	0.147	0.018	0.12	0.1
Cl	32.4	32.8	24.9	32.0	400.0
SO_4	25.8	0.03	9.0	12.3	250.0
Si	0.9	0.56	0.44	0.37	NS
pH	7.7	7.39	7.5	7.84	5.5-9.5

All concentrations are in mg l^{-1}
n=number of samples
NS=No Standard

Bottrill (1994) of some Warwickshire rivers, both Si and SO_4 would appear to be high, but the value is still 22% of the maximum PCV for potable water.

There would not appear to be any likelihood of remobilisation of heavy metals bound to sediments as long as environmental conditions remain stable.

4.6 Summary

Swanswell Pool is a shallow, freshwater lake which contains up to 3.0 m of sediment. At an average depth of about 50 cm in the sediment column is a transition from black organic gyttja to a red minerogenic clay. The supposition that the red clay / gyttja boundary represents the isolation of Swanswell Pool from its catchment is further confirmed by palaecological evidence of the trends in Mollusca. The visual stratigraphy is confirmed by mineral magnetic measurements which indicate the greater haematite content in the red clay and the predominance of magnetite, possibly as MD particulate pollutants, in the gyttja. The red clay therefore represents material which accumulated whilst the Springfield Brook flowed into the Pool and comprises catchment-derived sediment. The black organic gyttja has accumulated since the channelization of Springfield Brook and the only possible source for this is the atmosphere with small amounts of runoff from the surrounding park.

The upper sediments show an increase in heavy metals up core. Since Swanswell Pool has had no channelled inflow since 1850, the majority of this is mainly derived from the atmosphere with some contribution from urban runoff. Trends in

heavy metal concentrations indicate increasing anthropogenic release of these elements. Sequential extraction emphasises the importance of Fe and Mn oxides and organic matter in the incorporation of metals into the sediment. Organic matter indicates a highly productive lake, although P concentrations do not suggest eutrophication problems. Sigg (1987) suggested that the main scavengers of heavy metals are probably falling particles, the high nutrient content of the sediments and high values for suspended sediment and PO_4 in the lake water indicate that there is no shortage of particles available for the sorbtion of heavy metals and their subsequent incorporation into the sediment.

Mineral magnetic measurements suggest that the upper sediments are dominated by multidomain pollution particles. This assertion is supported by ^{210}Pb data which has high ratios of supported to unsupported ^{210}Pb reflecting the dominance of the atmosphere in providing the sediment source.

The statistical analysis of the grid of cores from Swanswell Pool has shown that there is a high level of collinearity between the magnetic parameters and also between the individual heavy metals. The correlation between heavy metals and magnetic parameters is inconsistent, but scattergrams pick out at least two populations of samples representing the top and basal samples in the black gyttja. PCA indicates that heavy metals accounts for much of the variation in the data in the majority of the cores, although again this is inconsistent as magnetic parameters dominate in core M3.

Whilst ^{137}Cs has enabled a tentative date to be suggested for core M7 at Swanswell Pool, ^{210}Pb could not confirm this date. The flux of ^{210}Pb to the surface sediment samples at Swanswell Pool, however, show that the atmosphere dominates the source of ^{210}Pb. This was confirmed by comparison of activities from rural lakes in Midland England.

The lake water appears to be of good general quality for an urban area and present conditions do not imply any remobilisation of heavy metals into the water column is likely.

Chapter 5

The Wyken Pool.

5.1 Introduction

This chapter presents all the results obtained from the analysis of sediments retrieved from Wyken Pool and listed in Table 2.21. Analysis of samples from the surrounding catchment and of water quality are considered in Chapter 6. This chapter is set out in the following way:

1. The physical characteristics of the lake, such as bathymetry and sediment thickness are covered first in section 5.1, followed by a consideration of sediment type and macrofossil content in section 5.2. Sediment density and organic matter content follows the stratigraphic descriptions and are given in section 5.3.

2. Section 5.4 presents both the spatial and downcore variations in lake-sediment chemistry beginning with a consideration of phosphorus concentrations in section 5.4.1. Section 5.4.2 examines the heavy metal distribution by analysing both total heavy metal concentrations and partitioning of heavy metals using sequential extraction.

3. Results of mineral magnetic analysis follows in Section 5.5 with ^{137}Cs and ^{210}Pb dating covered in section 5.6. Particle size is discussed in Section 5.7.

4. Statistical analysis of the results from Wyken Pool including correlation, regression and Principal Component Analysis are presented in Section 5.8.

5.2 The characteristics of Wyken Pool and of its lake sediments

5.2.1 Bathymetry and sediment thicknesses

A bathymetric map, contoured from hand line depth measurements, is given in Figure 5.1. The maximum depth of water, 1 m, was recorded at an isolated point near the landing stage, with 0.9 m recorded at the north eastern margin, and 0.8 m in the southern quarter of the lake. Over much of the rest of the lake, water depths varied between 0.5 and 0.75 m. On the day of measurement a head of 4 cm of water was recorded at the downstream weir plate and all depths were adjusted to 0 cm on this weir.

Sediment thicknesses to the former soil surface underlying the lake sediment were measured with survey rods and are presented as an isopach map in Figure 5.2. The thickest sediment lies in the eastern half of the Pool, with the deepest point in the southeast near the southern end of the marsh. The sediment becomes gradually shallower to the western shore, with a thicker wedge of sediment extending from the inlets down the eastern shore in the form of a submerged delta. Figure 5.3a combines water and sediment depth data for cross sections in the Pool and Fig 5.3b shows a contour map of the original lake bottom with the sediment removed. This

Fig 5.1 Bathymetry of Wyken Pool

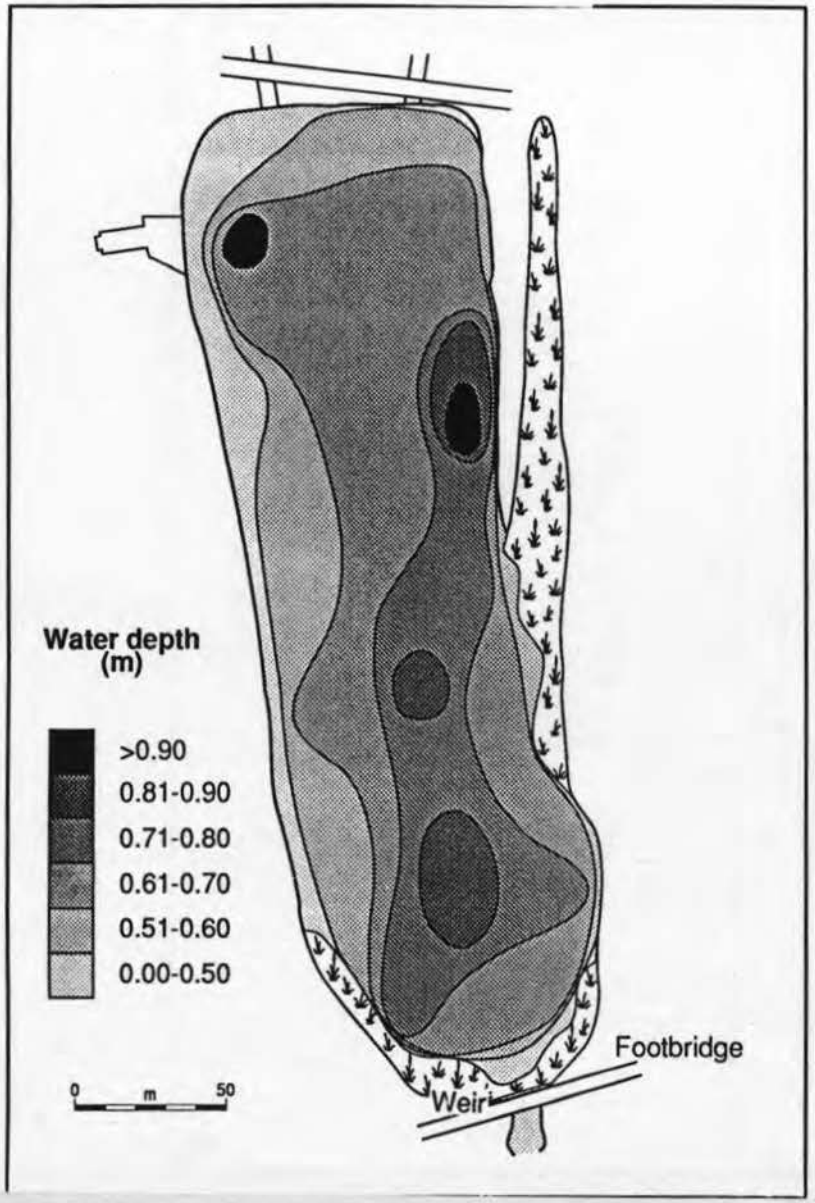


Fig 5.2 Sediment thickness

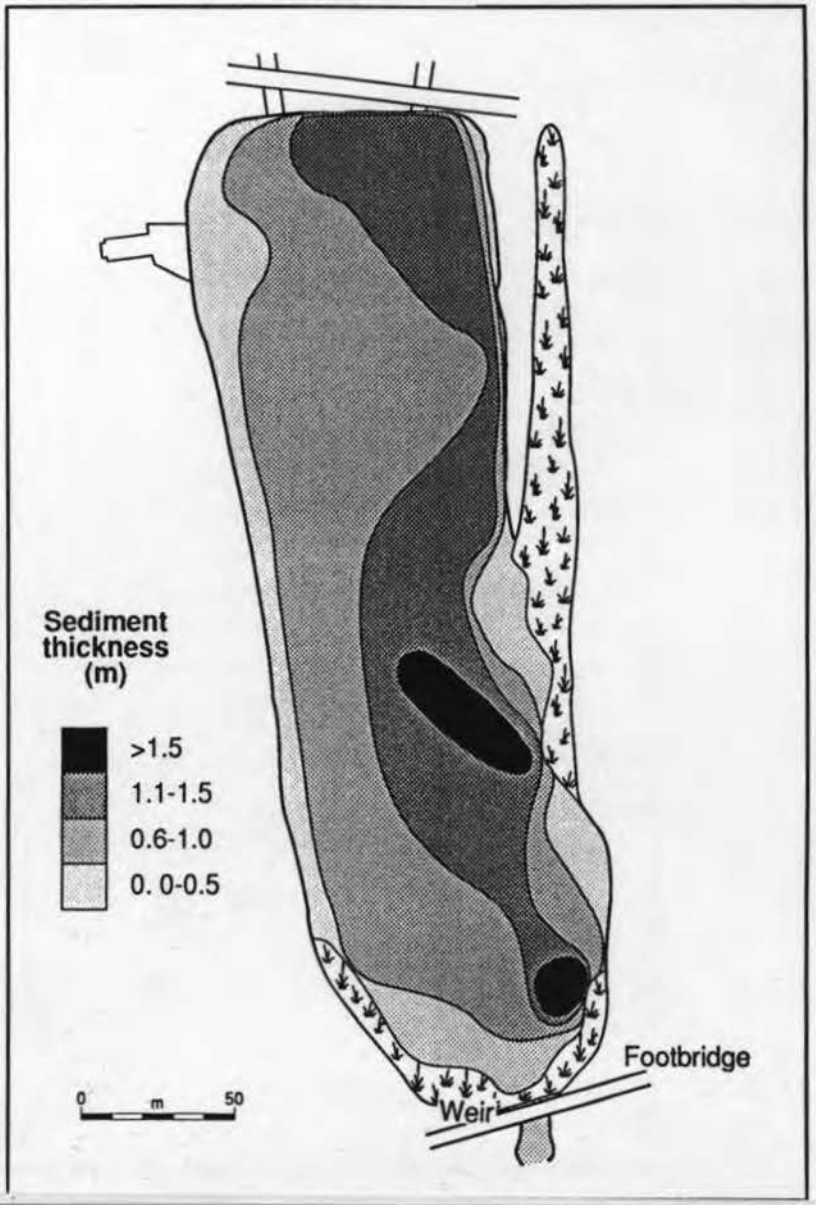
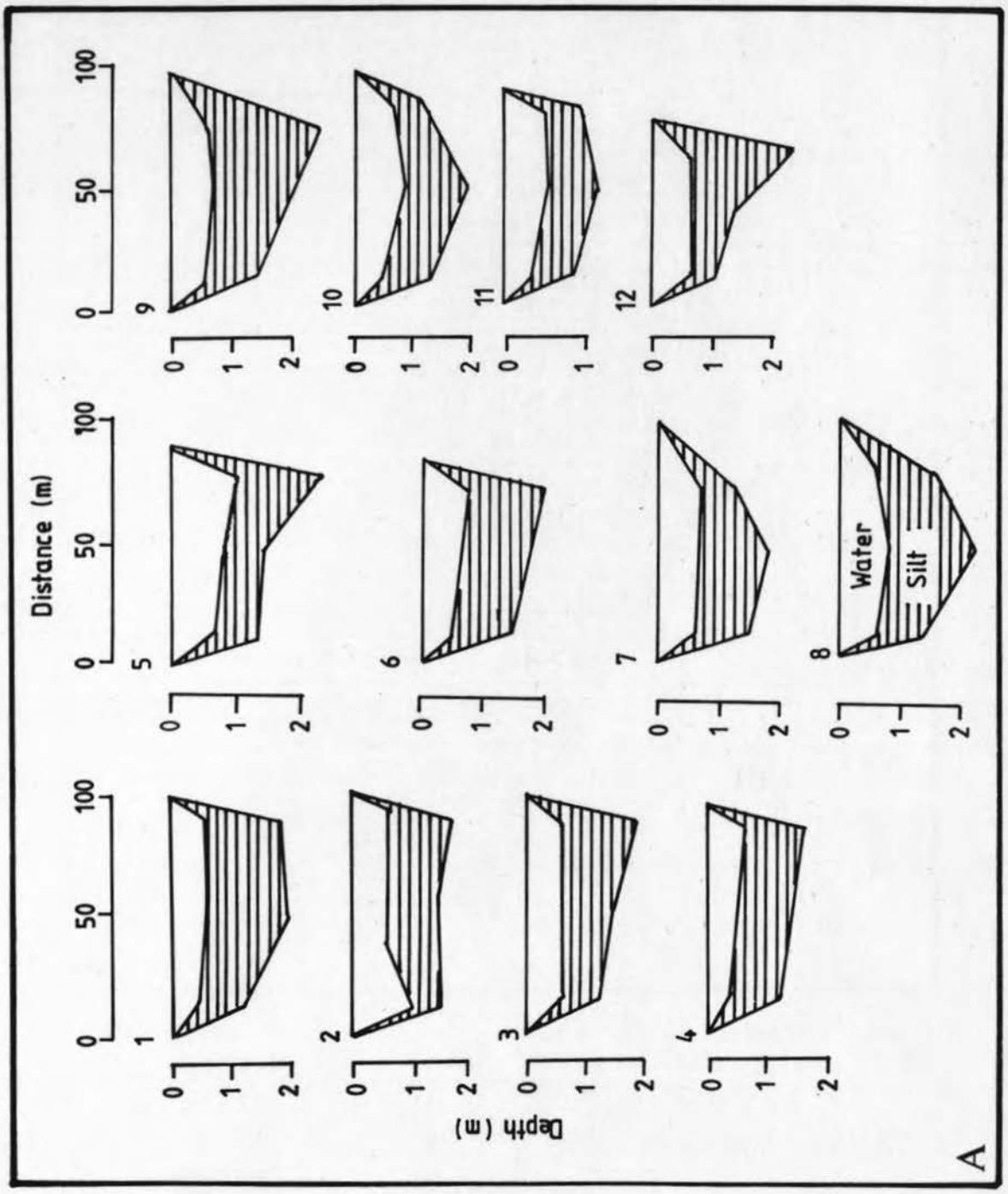
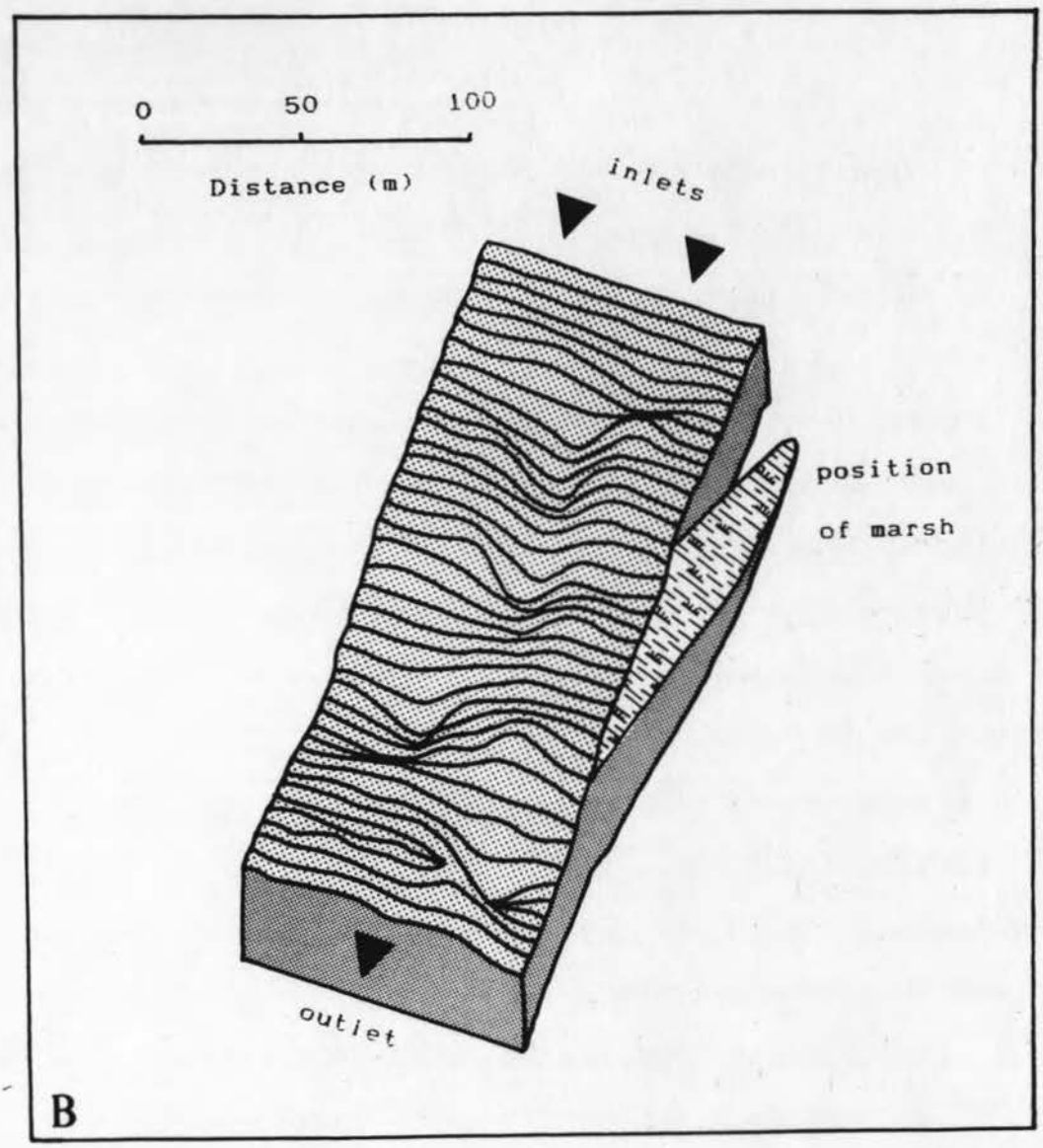


Fig 5.3 a. Cross-sections of Wyken Pool to show sediment depth
b.A block diagram of Wyken Pool with both water and sediment removed showing the former soil surface




0
50
100
Distance (m)
inlets
position
of marsh
outlet
B

demonstrates a sinuous asymmetrical depression traversing the Pool from north to south which may represent the position of the original stream before subsidence (Fig 3.9a).

5.2.2 Core stratigraphies

The stratigraphy of the cores taken from Wyken Pool are presented in two Figures. Figure 5.4 shows the sediment type found in the Pool and 5.5 shows the macrofossils present in the cores.

The sediments were a uniform black to grey-black organic gyttja comprising fine silts and clays. There were distinct bands of molluscan remains in addition to plant debris. At the base of the lake sediment along transects A, B and C, nearest the eastern margin of the Pool, and along transect D nearest the western margin was a dense mat of filamentous algae, whose preservation was too poor for identification to be made. In core B1, this mat contained large numbers of mollusc shells. The filamentous alga appeared throughout the cores in distinct horizons. Beneath the algal mat, and marking the base of the lake sediment, was a layer of grass and dry, friable soil of the original land surface before subsidence produced the depression which became Wyken Pool. Other plant remains included leaves which were found in cores around the edges of the Pool, particularly the western side, in cores A3, A2, C3 and D2. The leaves were not particularly well preserved, but appeared to be of the Great Reedmace, or bulrush, *Typha latifolia*. Evidence of one of the Stoneworts, either *Nitella flexilis* or *Chara vulgaris*, was found in core C1 with the

Fig 5.4 Lake sediment type at Wyken Pool

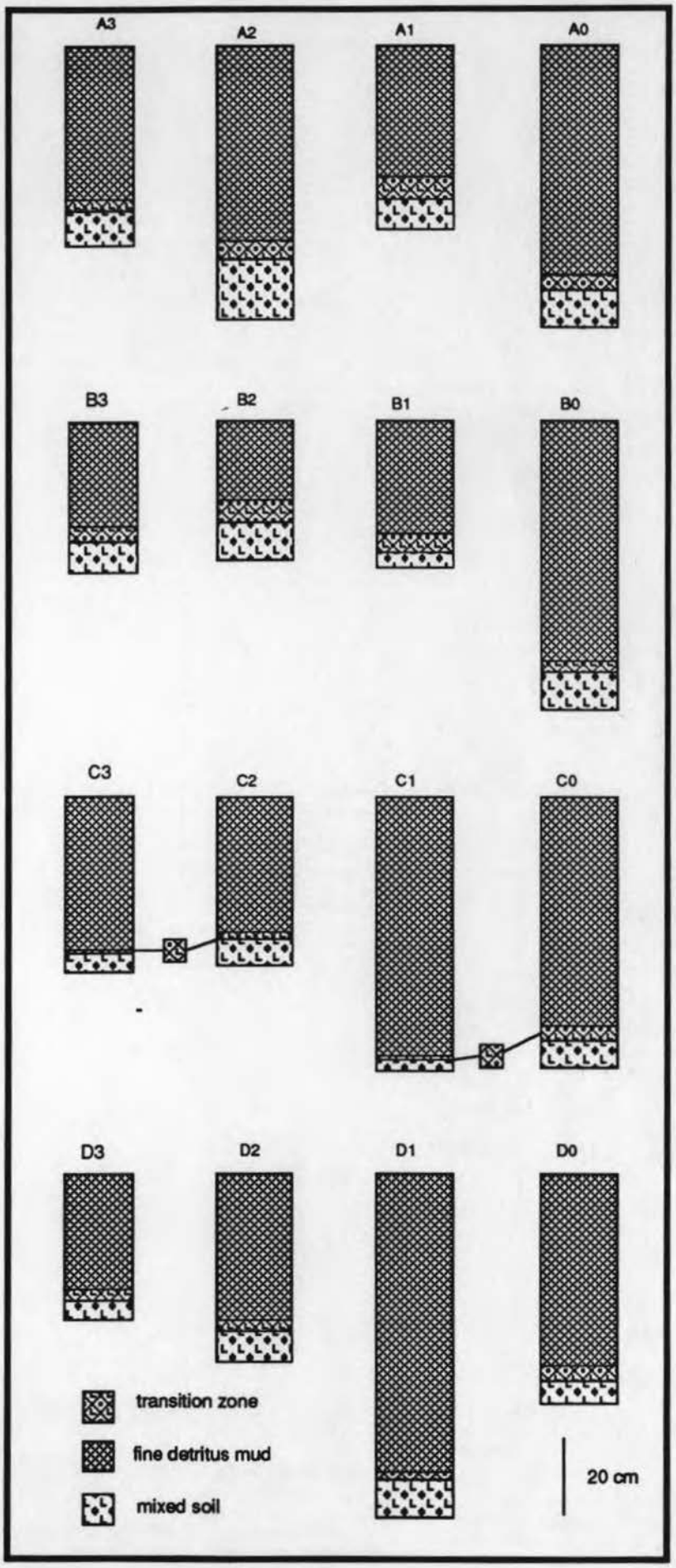
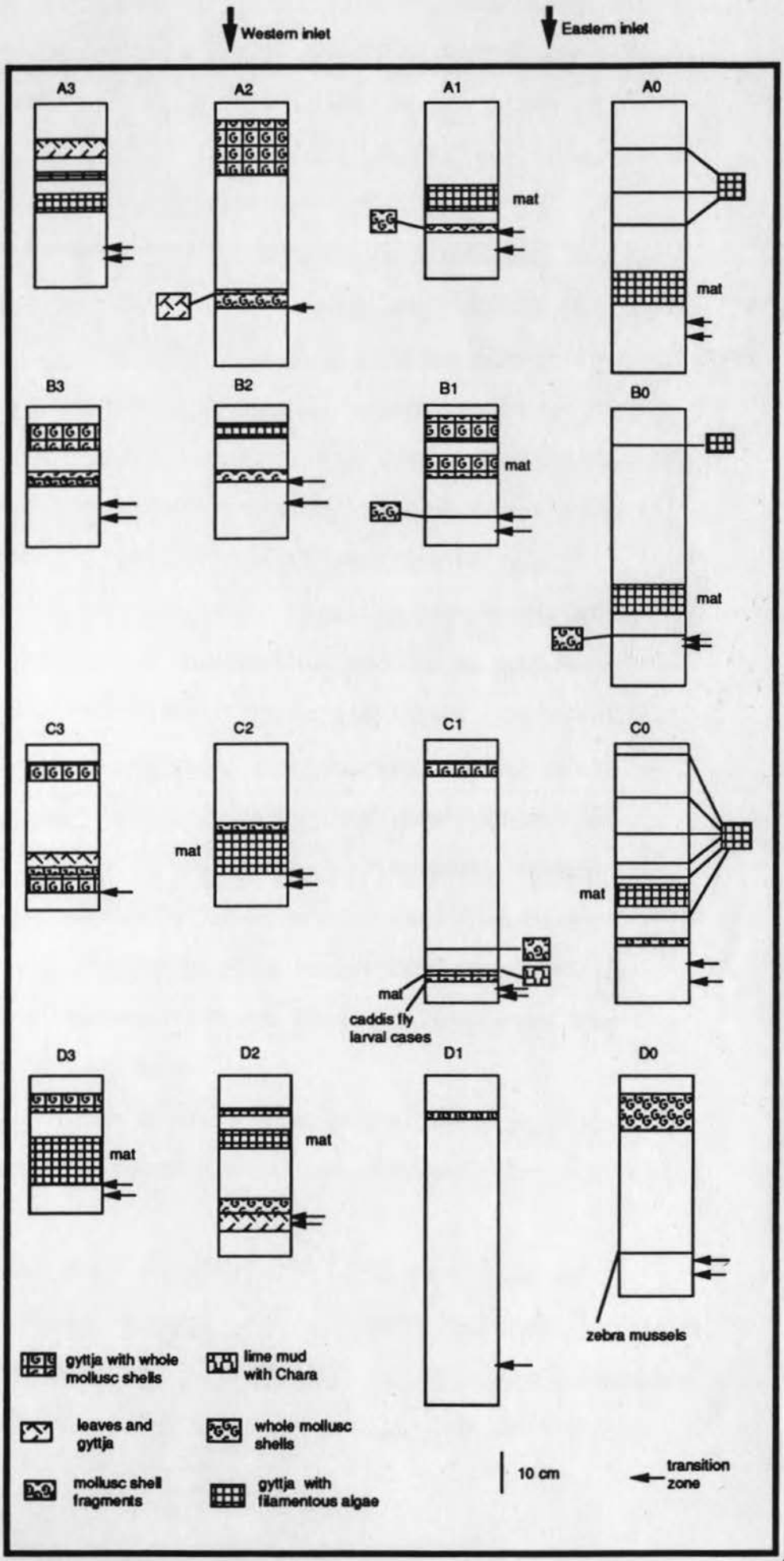


Fig 5.5 Macrofossils in the sediments from Wyken Pool (based on the Troels-Smith (1955) classification scheme)



presence of lime coating the stems of the plant found in the sediment directly above the algal mat. Below the algal mat in the same core were several Trichoptera larval cases (possibly *Setodes argentipunctella*). These were small, 0.6 cm in length, and had a smooth coating of sand grains.

There were distinct layers of molluscs present in the cores, but of variable extent and thickness. Sometimes they occurred in association with the filamentous algae. There were also some isolated mollusc specimens. Whole mollusc shells were not present in large numbers, but preservation was good. Several very well preserved specimens of the Zebra Mussel, *Dreissena polymorpha*, were found in core D0 in the southwestern corner of the Pool. These occurred above the former soil at a depth of between 48 and 52 cm and were present in association with filamentous algae. In one case conjoined valves were present, and the alga could still be seen adhering to one of the shells. The Zebra Mussel was introduced into the UK in the early nineteenth century in Rotherhithe Docks, probably attached to floating timber (Strickland, 1838). It had spread to the Avon by 1837 and therefore provides confirmation of the earliest date for the sediments in which they were found.

Table 5.1 lists the Mollusca recovered in a grab sample from near the western inlet (Site 1) and from near the outlet stream (Site 2).

Sample one was poor in Mollusca, yielding only 46 individuals of 4 taxa. Sample two was more prolific, with 304 shells of 12 taxa present. All but two of the species present were of aquatic habitat. The two marsh species, *Carychium*

Table 5.1 Contemporary molluscan fauna from Wyken Pool. (After Foster *et al.*, 1988)

	Site 1	Site 2
Freshwater species		
Potamopyrgus jenkinsi (Smith)	-	2
Phsya fontanalis (Linné)	1	37
Lymnaea peregra (Müller)	35	183
Planorbis planorbis (Müller)	2	21
Gyraulus laevis (Alder)	-	2
Gyraulus albus (Müller)	-	6
Armiga crista (Linné)	-	1
Hippeutis complanatus (Linné)	-	30
Sphaerium corneum (Linné)	8	9
Sphaerium lacustre (Müller)	-	14
Marshland species		
Carychium minimum (Müller)	-	1
Aegopinella nitidula (Drapernaud)	-	1

minimum and *Aegopinella nitidula*, inhabit water-side vegetation and may have been washed into the sediments. Also present in the samples were larval cases of Trichoptera and specimens of Ostracoda.

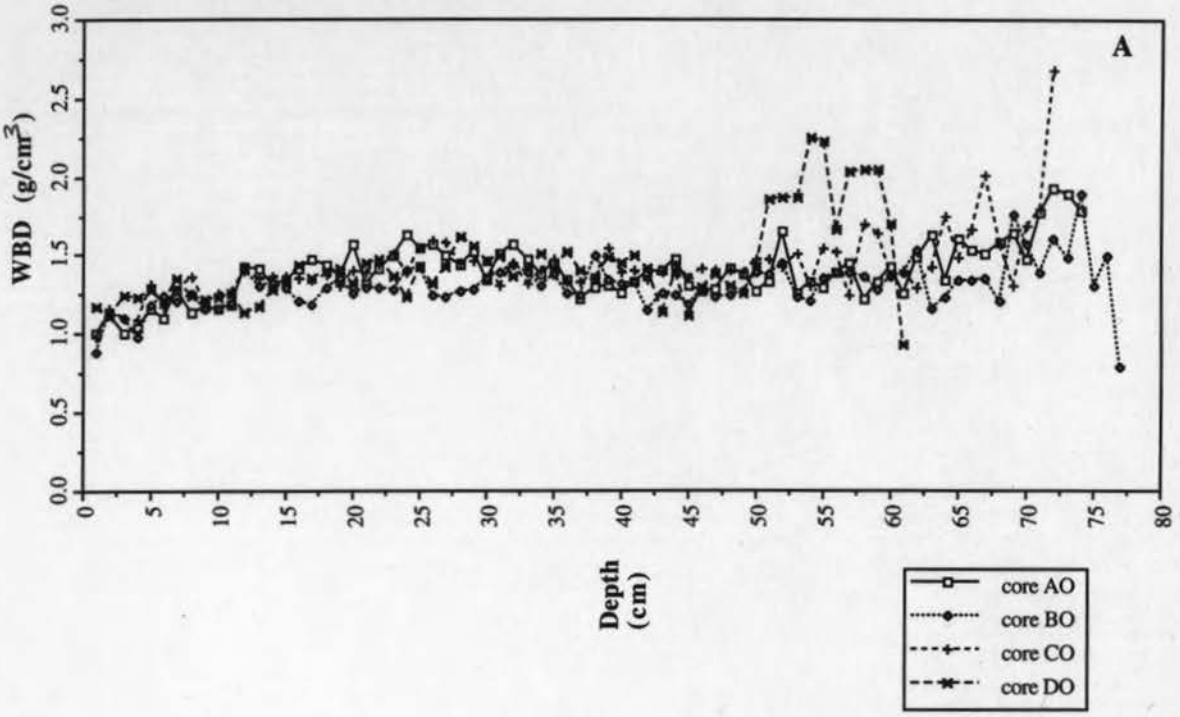
Pebbles were present in some of the cores. The average depth of the lake sediment in the cores was 48 cm.

Lying on top of the lake sediment across the whole of the lake was a thick layer of blanket-weed, *Cladophora glomerata*, (H. Smith, Biology Department, Coventry University, pers. comm.). This was coated in black, oily sediment and had an unpleasant smell. In association with the faunal and floral evidence presented in Chapter 3, it appears that Wyken Pool supports a reasonable diversity of life for an urban site.

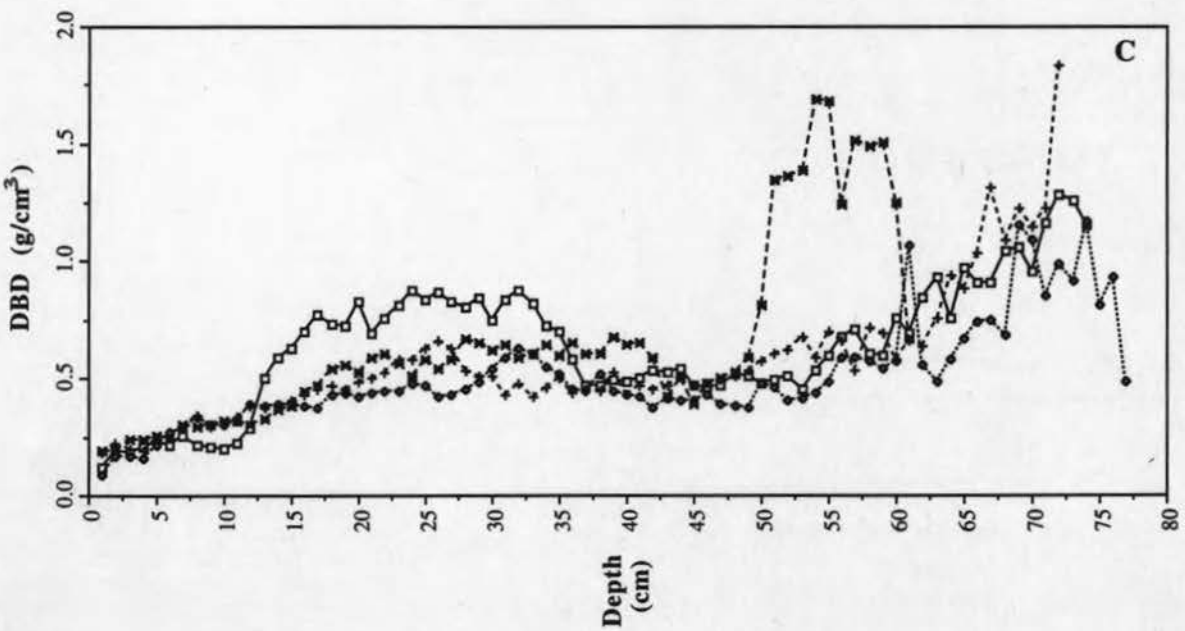
5.2.3 Bulk density and loss on ignition.

Wet densities (Fig 5.6 a) are very low in the cores, but increase downcore as interstitial water is removed under pressure from the overlying sediments. Maximum dry densities (Fig 5.6 b) approached 1.2 g cm^{-3}. Most cores demonstrate a significant rise in density downcore from about 11 cm in the A transect, nearest the inlet, and 31 cm in the B transect. This increase is much less easily identifiable in the C and D transects, further away from the inlets. The rise is followed by a decrease in density with increasing depth, and then the bulk density increases smoothly with depth to the base of the core at the soil/sediment interface. In a continuously sedimenting basin, the bulk density would be expected to decrease smoothly with depth due to the pressure of overlying

Fig 5.6 Downcore trends in bulk density
a. Wet bulk density b. Dry bulk density c. Dry : wet ratio



Depth of former soil surface
AO = 61 cm, BO = 65 cm, CO = 61 cm, DO = 51 cm



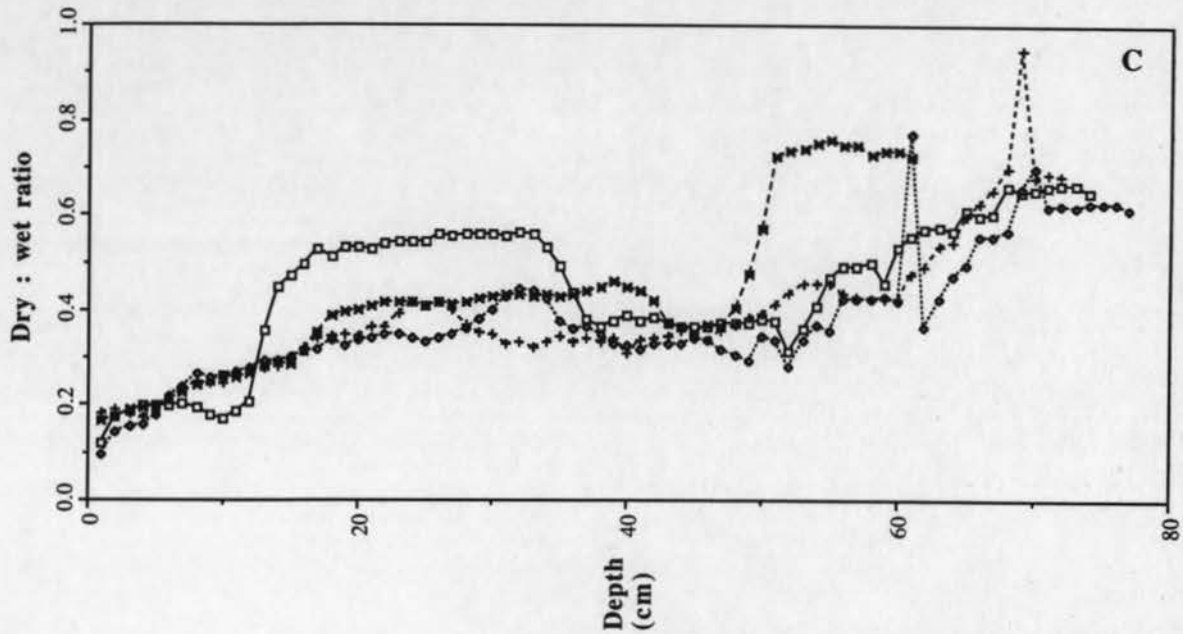
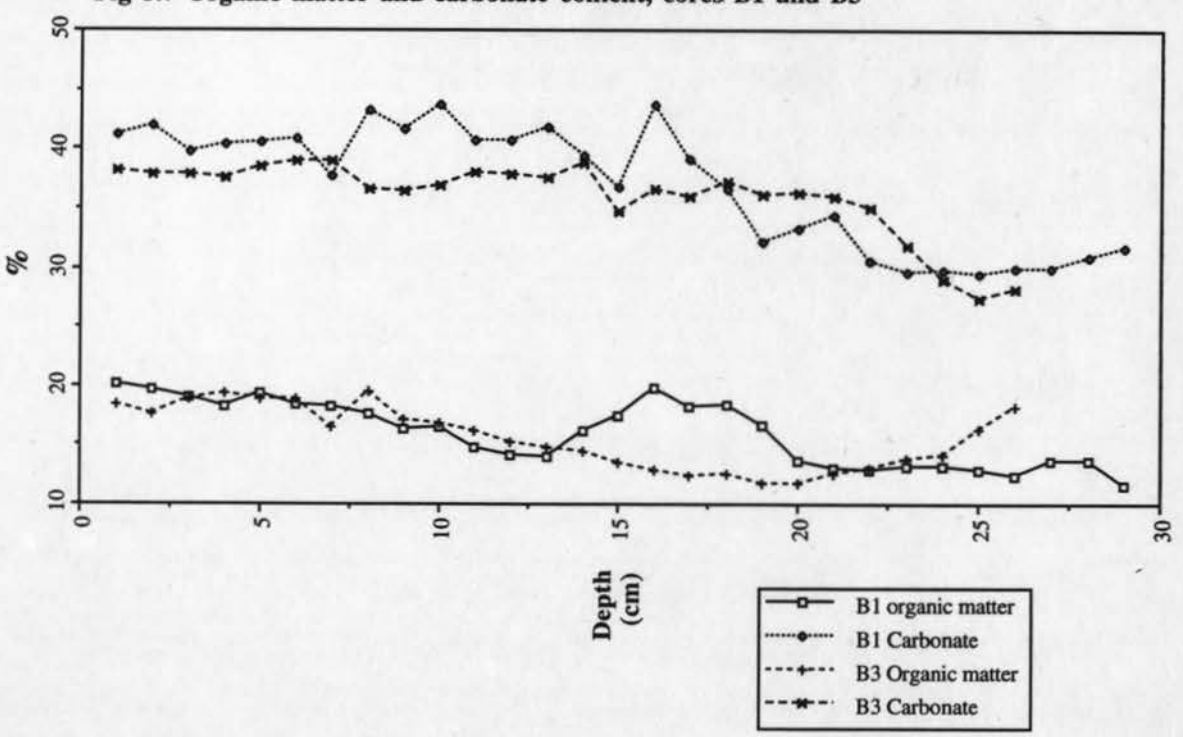


Fig 5.7 Organic matter and carbonate content, cores B1 and B3



sediments (Håkanson & Jansson, 1983). That this is not the case, in particular with reference to the A transect near the inlets, may indicate two possibilities (Foster *et al.*, 1990):

1. There may have been an influx of dense sediment into the lake. This may have been associated with catchment disturbance and may date to construction activities upstream of the Pool, or to the excavation of the drainage ditch through the marsh in the 1970s (Chapter 3.4.2).

2. Foster *et al.* (1990), suggest that increases in density in lake sediments can be associated with the lowering of the lake water level and the subsequent drying out of the sediments upon exposure to the air. There is no evidence to suggest that this has occurred at Wyken Pool.

The ratio between dry and wet bulk density (Fig 5.6 c) clearly shows the area of higher dry bulk density in core A0 as the ratio rises to over 0.5 at between 12 and 36 cm depth. The dry : wet ratio also highlights an increase in core D0 at between 15 and 43 cm deep which is not so easily discernable on the traces of the individual parameters. Cores B0 and C0 show similar but smaller peaks between 21 and 27 cm, and 27 and 37 cm depth respectively. This suggests that the changing sedimentation rate is present down the whole length of the Pool, but is more marked on the A transect, near the inlets.

Percentage loss on ignition data for cores B1 and B3 are shown in Fig 5.7. The trends for organic matter in both cores are similar in that they both exhibit a general decrease

downcore, although core B3 does increase in organic matter content in the basal samples. The top sample of B1 has an organic matter content of 20%, decreasing to 11% in the basal sample. The decline is interrupted between 13 cm and 20 cm by a zone of slightly higher values, which reach a maximum of 20%. The top sample of core B3 has an organic matter content of 18% which gradually falls to a value of 11% at 20 cm before gradually increasing to 19% at the bottom of the core. Levels of organic matter in Wyken Pool are slightly lower than those in Swanswell Pool (Fig 4.7), but in comparison with other lakes in Midland England, such as Merevale Lake (0.75 - 5.9%) and Seeswood Pool (9.2 - 11.6%) (Foster *et al.*, 1987) are still high reflecting high catchment deliveries of organic matter, or high productivity in the lake.

Again, both cores show similar profiles for carbonate content with a general trend of decreasing carbonate content downcore. The top sample in core B1 has a value of 41%, which falls to a minimum of 29% in the basal sample. The top sample in core B3 contains 38% carbonate with little change until 15 cm depth when the carbonate content decreases towards the basal sample. Comparison of the levels of carbonate in the cores from Wyken Pool with those from Swanswell Pool show them to be intermediate between M4 and M11. There is no match between the stratigraphies and carbonate content except in the case of core B3 at between 15 and 19 cm depth where the algal mat is found.

5.2.4 Sediment Chemistry

The results of sediment chemical analysis is presented in the next section which is divided into three parts. The downcore trends in heavy metal pollution in the lake cores are presented first in order to reconstruct their delivery to the lake over time. The spatial distribution of heavy metals in the upper 1 cm of the lake sediments of the grid shown on Fig 2.7 b is also discussed in this section.

The second section examines the spatial and downcore distribution of P, Fe and Mn in their role as past redox and nutrient indicators (Chapter 2.11).

Finally, the third section is concerned with the non-metallic elements. As outlined in Chapter 4.2.4, these can be used to indicate past sedimentation regimes as well as changing salt concentration with time. Chapter 2.8 v discussed the release of heavy metals to the environment with changing concentrations of salt.

1. Heavy metals analysis

a. Trends in metal concentration with depth

This section is divided into two with a consideration of the analysis for total heavy metal concentration downcore presented first followed by a discussion of the results of a sequental extraction carried out on one lake core.

i. Total extract for heavy metals

A similar general trend is found in all the heavy metal profiles in the lake sediment cores. The upper sediments exhibit concentrations far higher than those in the basal sediments. Ni (Fig 5.8 a), however, shows the least variability apart from core D, where concentrations increase considerably between depths of 9 cm and 30 cm reaching a maximum of 210 $\mu g\ g^{-1}$ at 20 cm. Values range between 65 (core C) and 80 $\mu g\ g^{-1}$ (core D) in the top sediments to between 25 and 50 $\mu g\ g^{-1}$ in the basal sediments.

The profiles for all the heavy metals can be divided into three distinct regions:

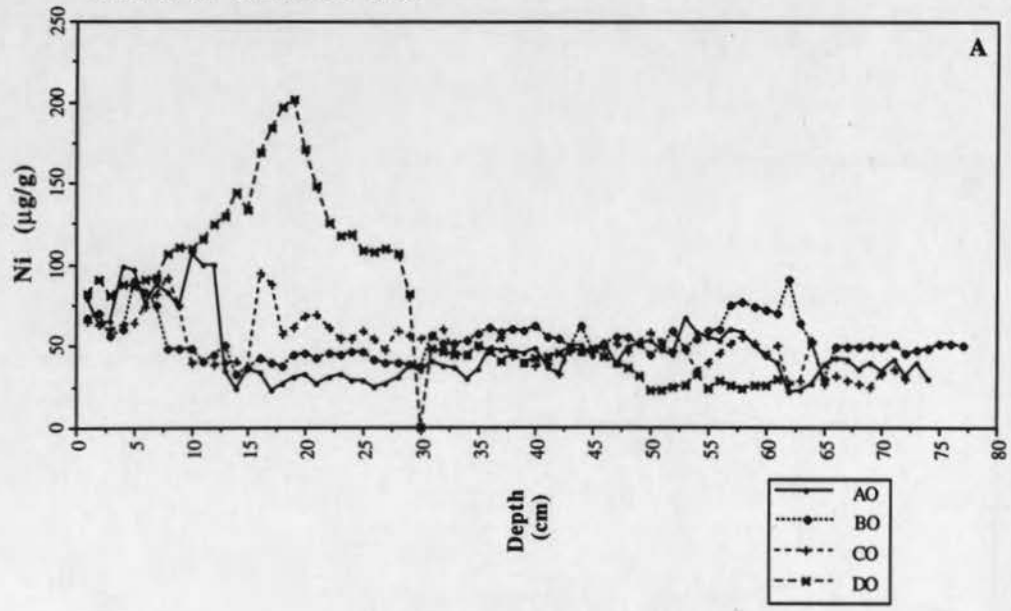
1. The upper third of the core contains samples with the highest concentrations of heavy metals

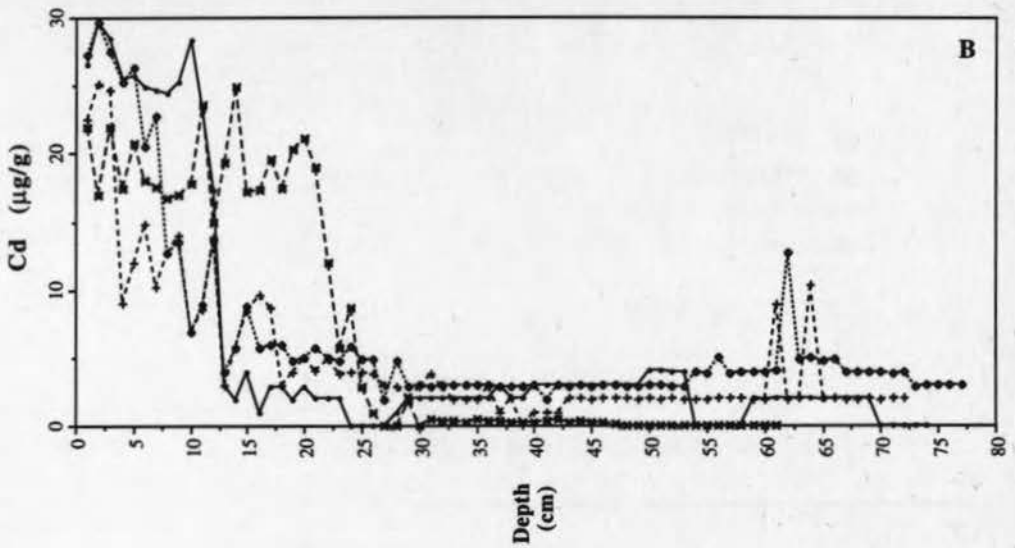
2. The central third of the core exhibits a gentle decline from the high concentrations in the upper samples

3. The lower third contains samples with the lowest concentrations of heavy metals and includes the basal soil, which also has low concentrations of heavy metals.

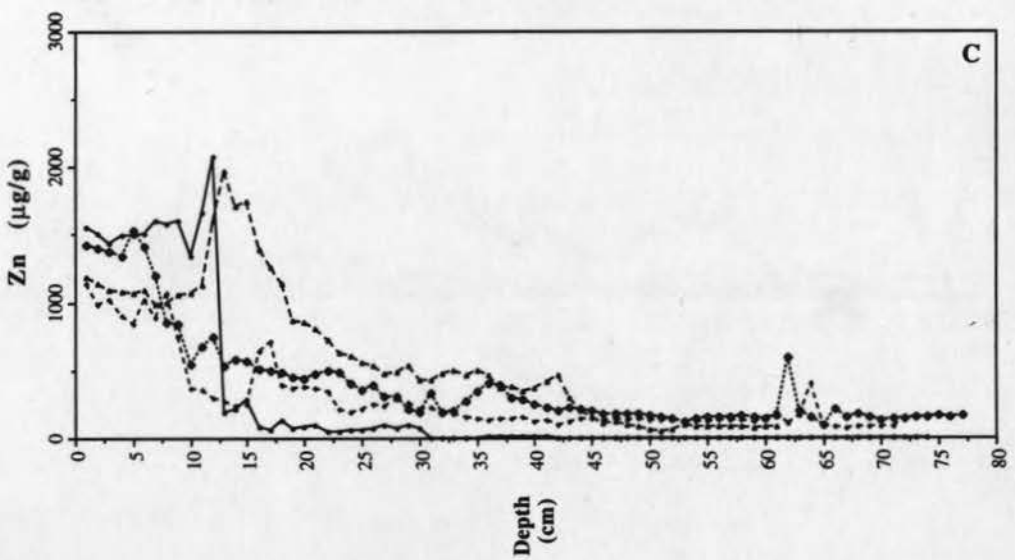
Maximum concentrations of 30 μg Cd g^{-1} (Fig 5.8 b) are found in the top samples of cores A and B; these levels are subsequently maintained to a depth of 24 cm in core D and 18 cm in the other three cores. Three isolated peaks occur at the bottom of cores B and C in both cases where the former soil

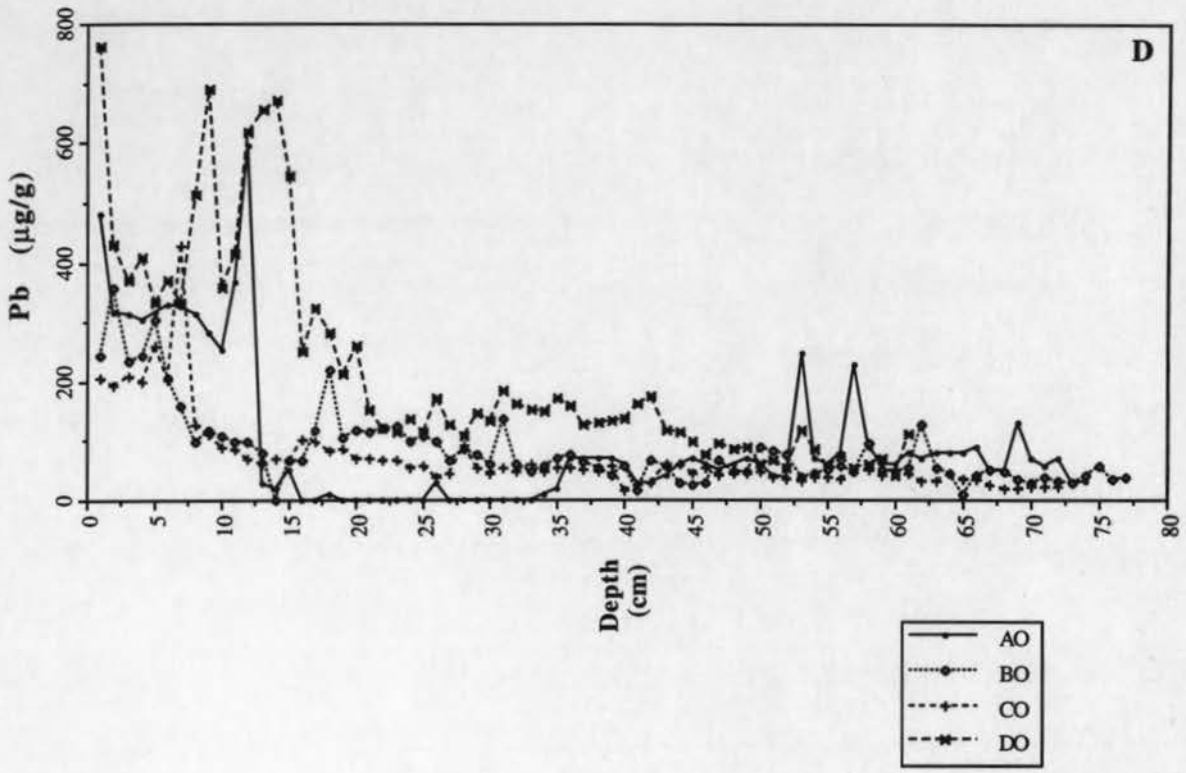
Fig 5.8 Total heavy metal content of lake sediment cores
a. Ni b. Cd c. Zn d. Pb e. Cu



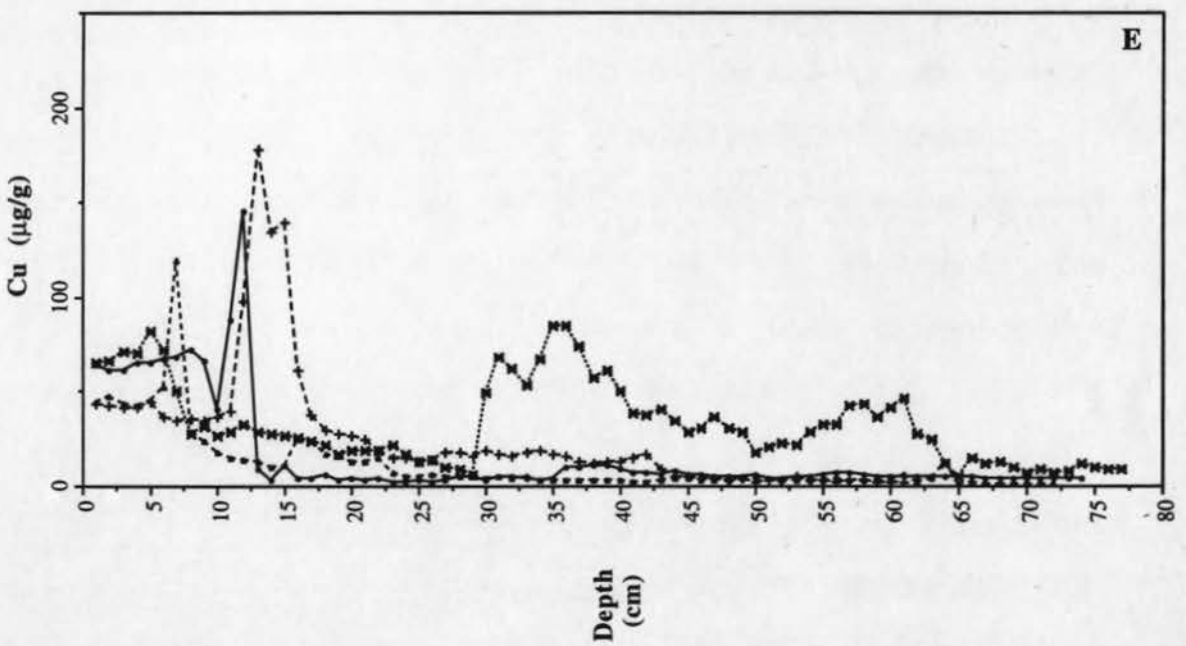


Depth of former soil surface
AO = 61 cm, BO = 65 cm, CO = 61 cm, DO = 51 cm





Depth of former soil surface
AO = 61 cm, BO = 65 cm, CO = 61 cm, DO = 51 cm



boundary is reached. Once the initial peak at the top of the cores has declined, values for core D from 30 cm depth are below the limits of detection. Values in the basal sediments of the other cores vary from 2 to 5 $\mu g\ g^{-1}$.

The upper 10 cm of cores B and C and the upper 19 cm of cores A and D contain the highest concentrations of Zn (Fig 5.8 c), ranging from a maximum of 2200 $\mu g\ g^{-1}$ in core A to 1200 $\mu g\ g^{-1}$ in core C. This upper peak in concentration decreases rapidly within 5 cm to the central third of the profile in which the gradient of the subsequent reduction in concentration is far less steep. Values for Zn in this second region vary from 500 to 100 $\mu g\ g^{-1}$ in cores A and D respectively. The lower third of the profile contains the lowest concentrations of Zn and extends from 16 cm depth in core A, 46 cm in core D, with cores B and C intermediate between these two depths. Zn values in core A reach minimum detection limits at a depth of 31 cm. Concentrations in the other three cores range from 50 to 200 $\mu g\ g^{-1}$.

The highest concentrations of Pb (Fig 5.8 d) are in the upper 8 to 20 cm of the profile, depending on the core. Maximum values approach 770 $\mu g\ g^{-1}$ in the top sample of core D and fall to less than 100 $\mu g\ g^{-1}$ in the basal sediments. Two isolated peaks occur in core A at 53 and 57 cm depth just above the boundary with the soil at 61 cm.

Maximum concentrations of Cu (Fig 5.8 e) occur in the uppermost 19 cm, with the highest value of 178 $\mu g\ g^{-1}$ in core D at a depth of 14 cm. Values below 19 cm are comparatively low in all the cores except core D in which a slightly higher value is maintained to a depth of 43 cm. Two isolated peaks

occur in cores B and C at 62 and 64 cm depth respectively; close to the junction with the buried soil surface. Table 5.2 summarises the maximum concentrations of heavy metals obtained from the Wyken Pool lake sediments.

Table 5.2 Maximum concentrations of heavy metals from the Wyken Pool lake sediments ($\mu g\ g^{-1}$)

Zn	Ni	Cu	Pb	Cd
2200	210	200	700	30

Like Swanswell Pool (Table 4.1), the heavy metal chemistry of the lake sediment is therefore dominated by Zn, followed by Pb, Ni and Cu with Cd present in lower concentrations. The core with consistently highest concentrations in all the metals is at location D, situated nearest the outlet. The initial peak is maintained to a greater depth in core D compared with the other cores. The concentrations of all metals in the top 1 cm sample of core D are no higher than those in the other cores, with the exception of Pb, where the concentration is up to 50% higher. Sediment thickness, Fig 5.2, shows that the eastern end of transect C and D contain the thickest sediment and hence may have been areas of net sediment deposition due to sediment focusing.

The trend of metal accumulation over time in Wyken Pool is of increasing concentration from above the soil surface found at the base of all cores, to the present day. As explained in Chapter 4.2.4, section 1 (ai), a background value is needed in order to assess the enrichment in the sediments due to anthropogenic activities. Chapter 3 suggests that the soil / gyttja boundary may represent about 1850 when the ground subsided to form Wyken Pool. This is further supported by Molluscan evidence (section 5.2.2) with the discovery of Zebra Mussels just above the soil in core DO which probably reached Midland England between about 1840 - 1850 (Strickland, 1838). The soil at the base of the cores therefore could provide samples from pre-1850 before the Industrial Revolution and before the onset of contamination by anthropogenic heavy metal release. Comparison of average heavy metal concentrations from the basal soil and published values (Förstner & Salomons, 1981) provides confirmation of the pre-Industrial Revolution origins of the basal soil from the Wyken Pool lake cores. Table 5.3 presents a comparison between background concentrations and average concentrations of heavy metals from Wyken Pool. This shows similar results to Swanswell Pool (Table 4.2) in that Zn, Ni and Cu are all comparable with the published data, but Pb, and particularly Cd are slightly higher. Since both sites are geologically similar (Chapter 3.2.1), this would seem to support the assumption that background values reflect local geology rather than any enrichment due to cultural effects. The basal soil was therefore used as a background value in any calculations of anthropogenic excess heavy metal delivery to Wyken Pool.

Table 5.3 Comparison between heavy metal concentrations in published background values of sediments and average values for the soil at the base of the lake sediments from Wyken Pool, in $\mu g\ g^{-1}$.

	1	2	3	4	5
Zn	105	115	118	95	90
Ni	51	46	66	68	40
Cu	25	51	45	45	20
Pb	16	30	34	20	40
Cd	0.2	0.3	0.4	0.3	2.0

1. Fossil lake sediments (Ries Lake n=25)
2. Fossil river sediments (Rhine n=4)
3. Recent lake sediments from remote areas (n=87)
4. Shale standard

Source: Förstner & Salomons (1981)

5. Soil at the base of Wyken Pool (n=40)

Chapter 4.2.4 section 1 (ai) discussed the calculation of enrichment factors for Swanswell Pool and these have been calculated for Wyken Pool and are presented in Table 5.4. Maximum values were taken from Table 5.2 and background values from the basal soil in lake sediment cores given in Table 5.3. All metals are significantly enriched, particularly Zn. Also given in Table 5.4 are the F values for Swanswell Pool and for

two lakes in the USA, Washington and Erie (Förstner & Wittmann, 1981).

Table 5.4 Cultural enrichment factors (F) for Wyken Pool compared with Swanswell Pool and Lakes Washington and Erie.

	1	2	3	4
Zn	55.4	22.4	4.0	6.0
Ni	2.6	5.25	nd	4.5
Cu	20.0	10.0	3.0	4.0
Pb	11.0	17.5	20.0	nd
Cd	22.5	15.0	nd	17.0

1. Swanswell Pool lake sediments
2. Wyken Pool lake sediments
3. Lake Washington lake sediments (compiled by Förstner & Wittmann, 1981)
4. Lake Erie lake sediments (compiled by Förstner & Wittmann, 1981)

nd = no data available

The sources of heavy metals to Lake Washington are from smelters and coal-fired plants as well as heavy traffic, whereas Lake Erie is subject to industrial pollution by chemical plants and electro-plating. Zn and Cu are more

enriched in the UK sites than the USA lakes, but the F value for Pb is higher for Lake Washington than for either of the UK sites. This illustrates the site-specific nature of the data obtained from lakes whose catchments have been subject to their own unique anthropogenic pressures. Jennett *et al.* (1980) suggest that due to the complexity of the systems studied, heavy metal behaviour may be ecosystem-specific. Table 5.5 compares heavy metal concentrations from Swanswell and Wyken Pools with lakes in areas subject to a variety of activities, such as mining and agriculture.

Table 5.5 shows that remote rural sites, such as Big Pool and Porth Hellick on the Isles of Scilly (Foster *et al.*, 1991) are an order of magnitude lower in metal concentration when compared to urban lakes such as Wyken and Swanswell Pools and Holmer Lake in Telford, Shropshire (Gaskell, 1992). However, the urban lakes are themselves an order of magnitude lower in concentration when compared with lakes subjected to contemporary (Sudbury; Nriagu & Rao, 1987) or historical mining (Llyn Geirionydd; Dearing, 1992 and Coeur D'Alene; Horowitz *et al.*, 1993) in their catchments.

Chapter 6.7.2 examines F values for the catchment components at Wyken Slough and Chapter 7.4 puts these values into a wider perspective by examining the global increase in the use of heavy metals with metal accumulation rates from Swanswell and Wyken Pools.

Table 5.5 Total heavy metals concentrations ($\mu g\ g^{-1}$) in sediments from lakes with various activities in the catchment. Adapted from Foster & Charlesworth, 1995.

	Pb min:max	Cu min:max	Ni min:max	Zn min:max	Cd min:max
Wyken Pool	51:476	28:490	26:163	52:1000	3:29
Swanswell	66:312	26:292	75:140	60:3600	6:17
Big Pool[1]	tr: 15	13: 37	9: 20	52: 259	- -
P. Hellick[2]	tr: 10	9: 21	tr: 22	37: 93	- -
Merevale[3]	38: 78	64:114	62:144	53: 786	- -
Seeswood[4]	18: 62	33: 80	42: 63	63: 124	- -
Holmer[5]	153:407	15: 51	75:129	508:2045	10:21
Sudbury[6]	14:7700	nd	<30:6200	200:1400	nd
Geirionydd[7]	10:2000	5:4000	nd	6: 850	nd
Coeur D'Alene[8]	14:7700	9: 215	4: 36	63:9100	<1:157

1. Big Pool: closed coastal lagoon, Isles of Scilly, UK (Foster *et al.*, 1991)

2. Porth Hellick: coastal lagoon with small cultivated drainage basin, Isles of Scilly (Foster *et al.*, 1991)

3. Merevale Lake: inland reservoir with forested catchment, Warwickshire, UK (Foster and Dearing, 1987 a and b)

4. Seeswood Pool: inland reservoir with arable and pasture catchment, Warwickshire, UK (Foster and Dearing, 1987 a and b)

5. Holmer: urban balancing lake, Telford, UK, constructed in 1969 (Gaskell, 1992)

6. Sudbury: maximum recorded values from M^{c} Farlane or Silver Lakes near the Sudbury Smelters, Ontario. (Nriagu and Rao, 1987).

7. Llyn Geirionydd: historical mining of Pb and Zn ore in catchment. (Dearing, 1992)

8. Coeur D'Alene: historical mining in catchment. (Horowitz *et al.*, 1993).

ii. Sequential extraction of heavy metals from lake sediment cores

This section is discussed under two separate headings to discriminate between the partitioning of heavy metals in the sediments and also the overall trend of metal concentrations with depth in the sediment column. As stated in Chapter 2.8.2b and on Table 2.21, this is based on work originally carried out by Ambridge, 1989, but the raw data have been recalculated and redrawn.

1. Partitioning of heavy metals in the sediments of Wyken Pool

Table 5.6 lists the primary and secondary sinks within the sediment for the individual metals. Fe and Mn oxides dominate for Ni, Zn and Cd, probably in the form of cements, or coatings on grains, (Tessier *et al.*, 1979) whilst organic matter dominates for Pb and Cu. The dominant secondary sink is organic matter, for Ni, Zn and Cd, whilst for Pb and Cu, the secondary sink is in the residual minerals. There is no evidence to suggest any fundamental change in the partitioning of metals through time at Wyken Pool except in the case of Cd in which organic matter dominates in the upper 5 cm whereas concentrations in the Fe and Mn oxides are slightly higher than organic matter below 5 cm. The imortance of the affinity of organic matter for heavy metals is well documented (Förstner & Wittmann, 1981), but it is not known why only Cd should demonstrate this effect in the Wyken Pool core. Comparison of Table 5.6 with Table 4.4 which lists the

Table 5.6 Fractions associated with the highest proportion of metal in the upper zone

element	fractions
Pb	organic matter; residual
Ni	Fe and Mn; organic matter
Zn	Fe and Mn; organic matter
Cd	Fe and Mn; organic matter
Cu	organic matter; residual

fractions associated with the highest proportion of metals in the upper zone of a lake sediment core at Swanswell Pool shows slight differences. Organic matter appears as an important sink in all metals from Wyken Pool, but only for Pb and Ni at Swanswell Pool. Fe and Mn oxides are also important in both lakes, but only Ni and Zn are common to both. Cd and Cu have completely different dominant fractions in both lakes. Pb and Cu at Wyken Pool are present in appreciable amounts in the residual fraction whereas this does not appear to be as important in Swanswell Pool. In terms of release of heavy metals to the environment from the sediments at Wyken Pool, residual minerals, which are found in the crystal lattices of minerals in the sediment, would probably only be released upon complete destruction of the crystal itself (Tessier *et al.*, 1979), but those heavy metals associated with organic matter

and Fe and Mn oxides would be released should redox conditions change (Tessier *et al.*, 1979). Chapter 6.6 returns to the problem of heavy metal release from sediments into the overlying water column with a consideration of the water quality at this site.

2. Trends in sequential heavy metal concentration with depth in the sediments of Wyken Pool.

The fractionation of the lake sediments yielded profiles which can be divided into two zones. In the upper zone, concentrations of the metals are generally higher than in the sediments below. There are, however, fractions in which the concentrations of all metals varies little, if any, downcore. These are listed in Table 5.7.

Table 5.7 Fractions with no variation in heavy metal concentration downcore

element	fraction
Pb	exchangeable; carbonate; Fe and Mn
Ni	exchangeable
Zn	exchangeable; crbonate
Cd	exchangeable
Cu	exchangeable; carbonate; Fe and Mn

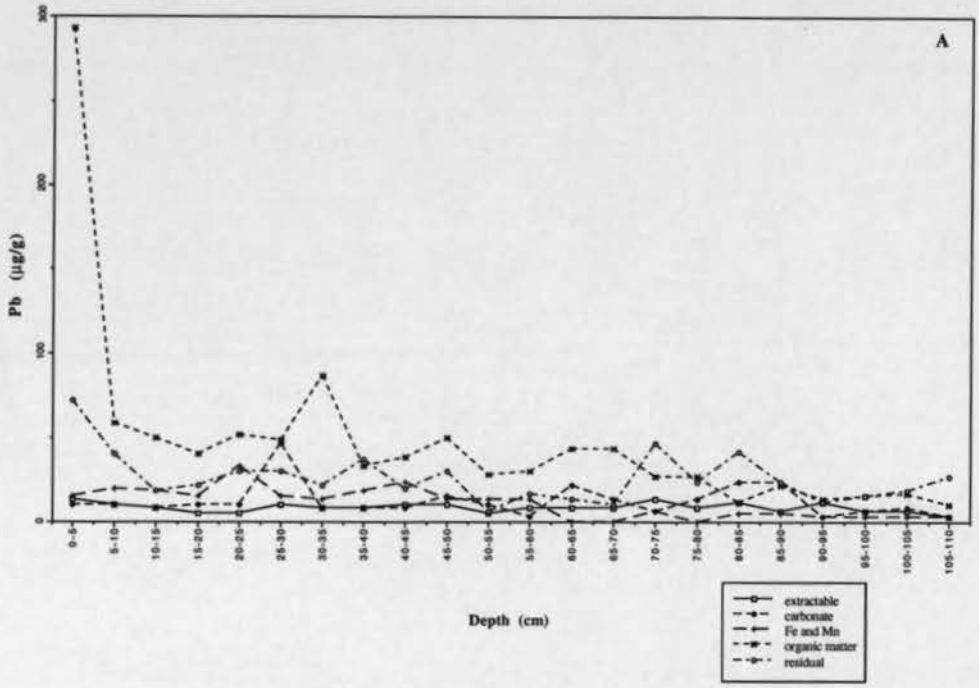
The trace for Pb (Fig 5.9 a) shows higher values in the top 3 cm and a gradual decline thereafter, apart from a peak in Pb associated with organic matter at a depth of 7 cm where concentrations reach almost 100 $\mu g\ g^{-1}$. The highest concentration is found in the fraction associated with organic matter where values approach 300 $\mu g\ g^{-1}$ in the top sample.

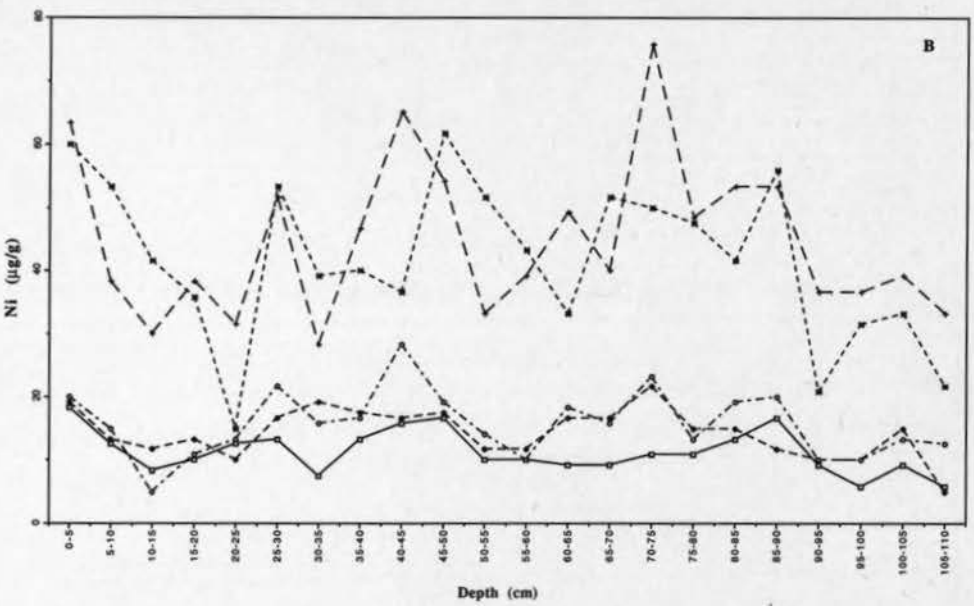
The distribution of Ni (Fig 5.9 b) between the five fractions is sharply divided. The higher concentrations, up to 80 $\mu g\ g^{-1}$, are found in the organic matter and Fe and Mn oxides, and these two are consistently higher than the remaining three fractions whose values vary between 30 and 5 $\mu g\ g^{-1}$. Whilst the lower 4 cm of the profile exhibits slightly lower values than the samples above, the Ni concentrations tend to fluctuate about the mean and a trend is difficult to identify.

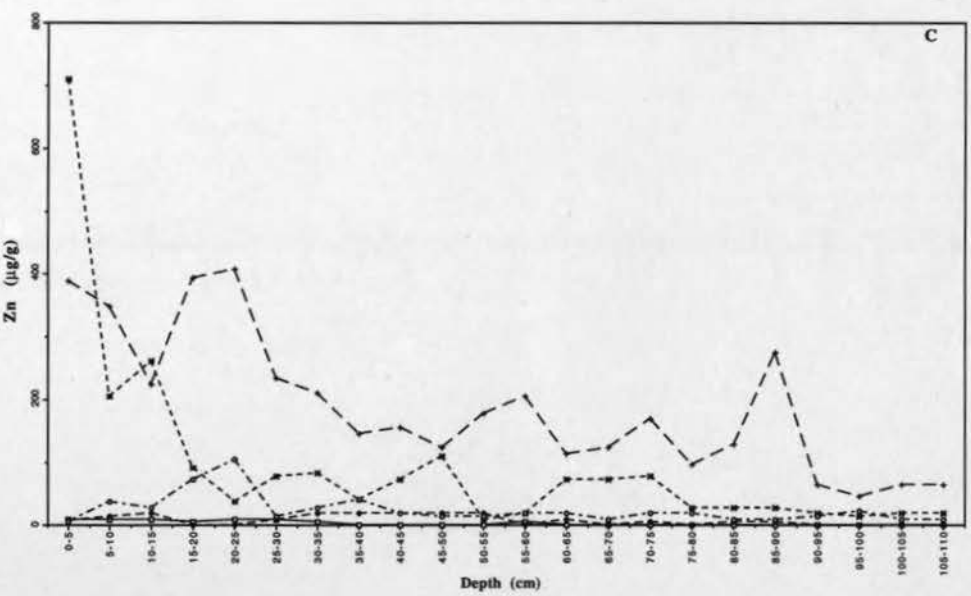
Zn bound to organic matter and Fe and Mn oxides clearly dominate the profile (Fig 5.9 c). The highest value is found in the organic matter where values reach over 700 $\mu g\ g^{-1}$. Values in these two fractions tend to decline with depth. Concentrations found in the remaining three fractions remain low, particularly the exchangeable and carbonate fractions, where values are mainly below the limits of detection.

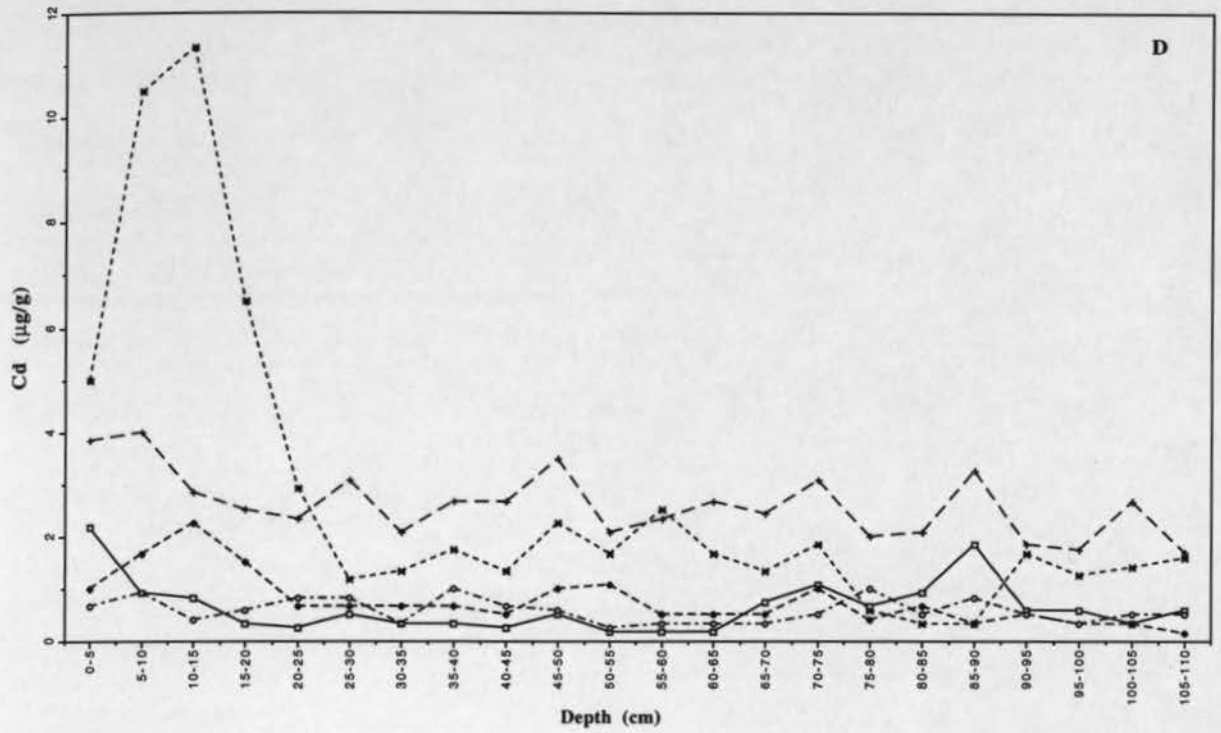
Cd bound to organic matter, Fe and Mn oxides and exchangeable Cd exhibit declining concentrations in the top 6 cm of the profile (Fig 5.9 d). Carbonates show a slight rise downcore. Below 6 cm depth, values for all the fractions remain constant. The highest concentrations are found in the organic matter fraction where they reach 18 $\mu g\ g^{-1}$ at a depth of 3 cm.

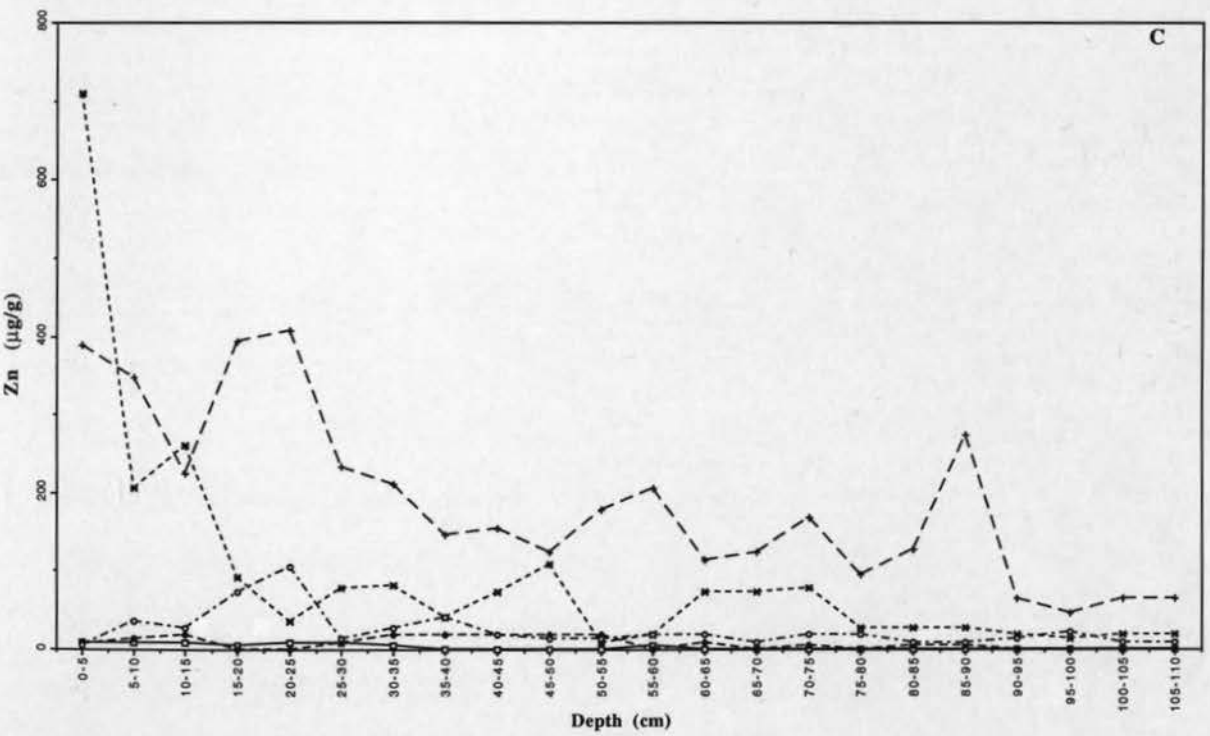
Fig 5.9 Sequential heavy metal extraction of lake sediment cores
a. Pb b. Zn c. Ni d. Cu e. Cd








D
Cd (µg/g)
0
2
4
6
8
10
12
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
50-55
55-60
60-65
65-70
70-75
75-80
80-85
85-90
90-95
95-100
100-105
105-110
Depth (cm)


C
Zn (µg/g)
0
200
400
600
800
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
50-55
55-60
60-65
65-70
70-75
75-80
80-85
85-90
90-95
95-100
100-105
105-110
Depth (cm)

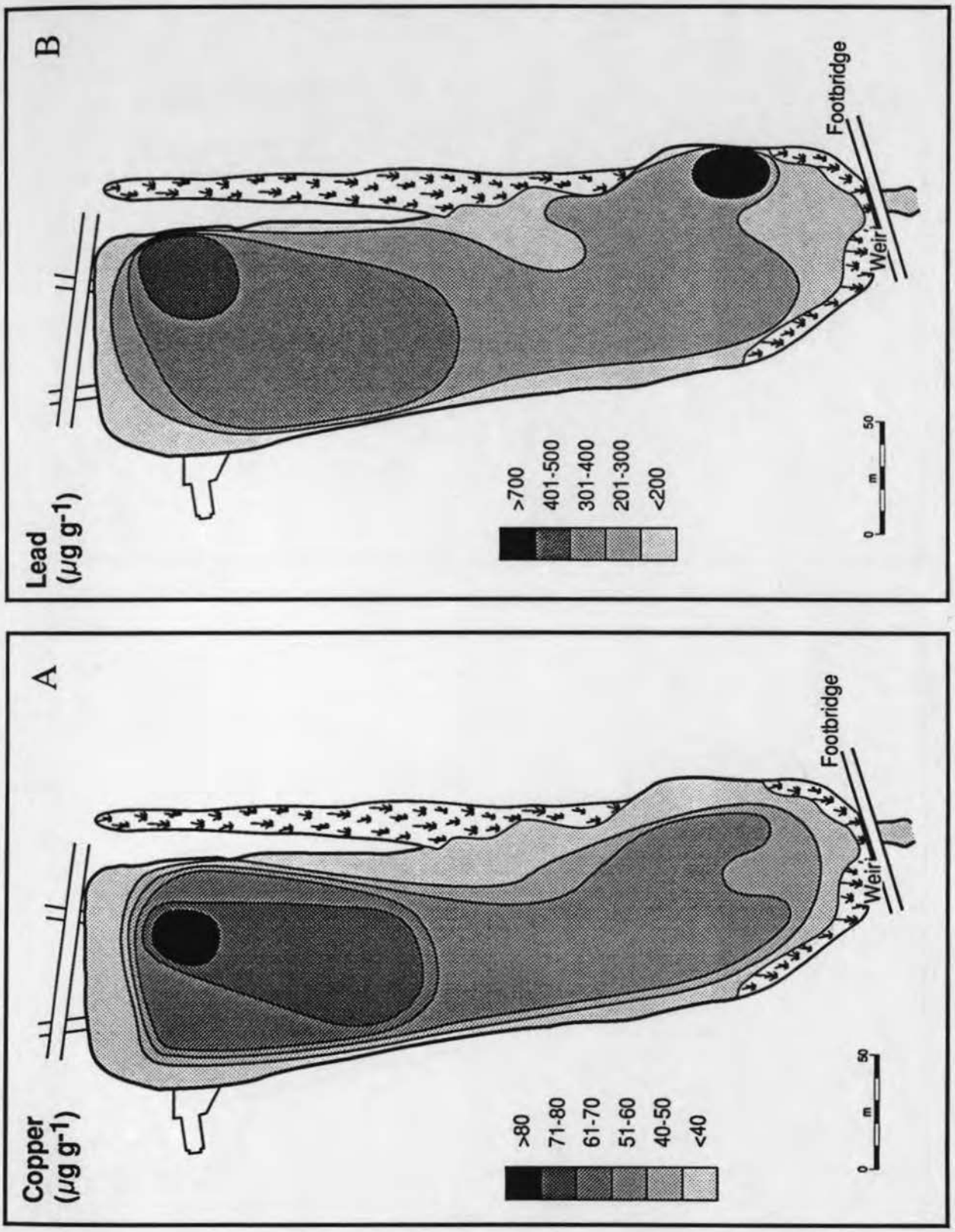
Exchangeable Cu, and that proportion bound to the carbonate and Fe and Mn oxide phases, exhibit little change down the profile (Fig 5.9 e); all values consistently register less than 3 $\mu g\ g^{-1}$. Cu bound to organic matter and in the residual phase declines from the highest concentration in the top 11 cm (30 and 12 $\mu g\ g^{-1}$ respectively in the top sample), to less than 1 $\mu g\ g^{-1}$ in the bottom 5 cm of the core.

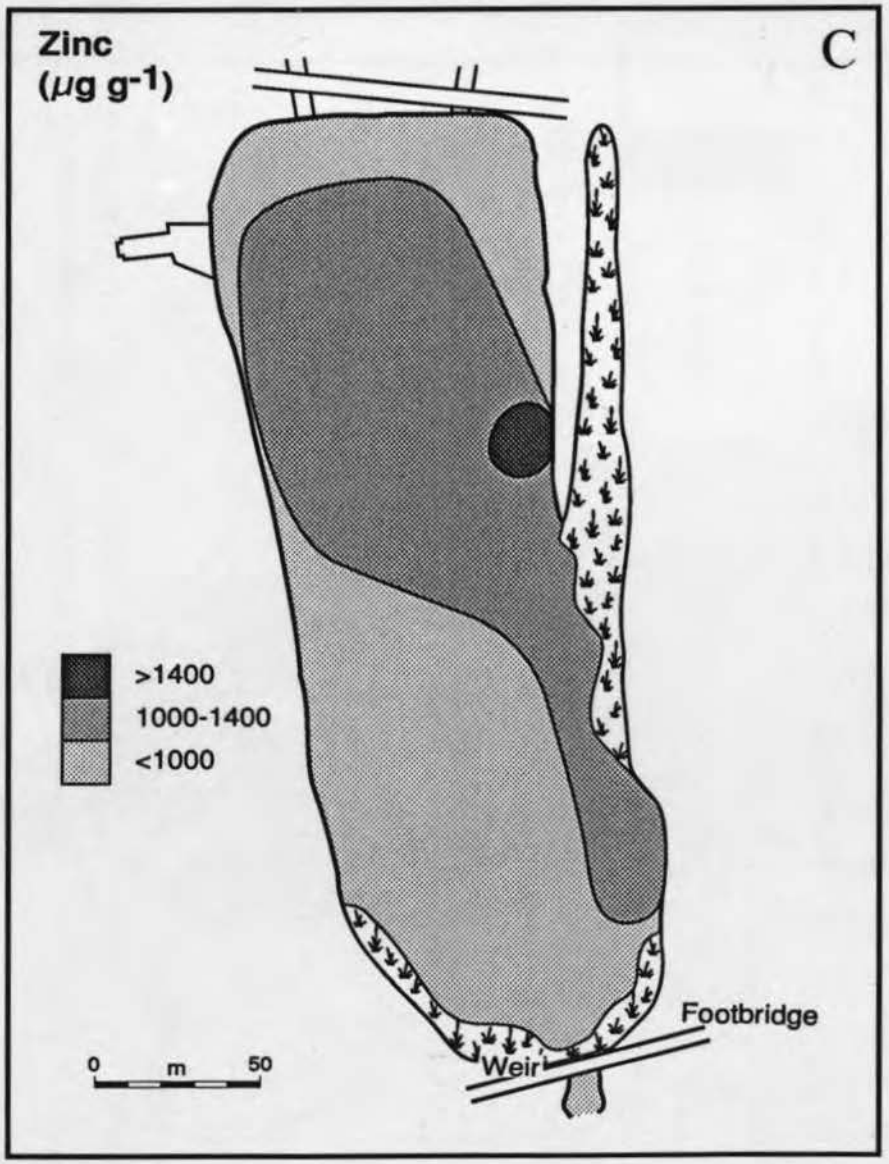
The overall trends of the sequential extractions reflect those found in the total extraction: that of increasing metal concentration towards the present day. However, the profiles do not resolve into the three zones shown in the total extractions. This may be because the core was taken from the C transect where the dilution effect in the middle of the core was less pronounced.

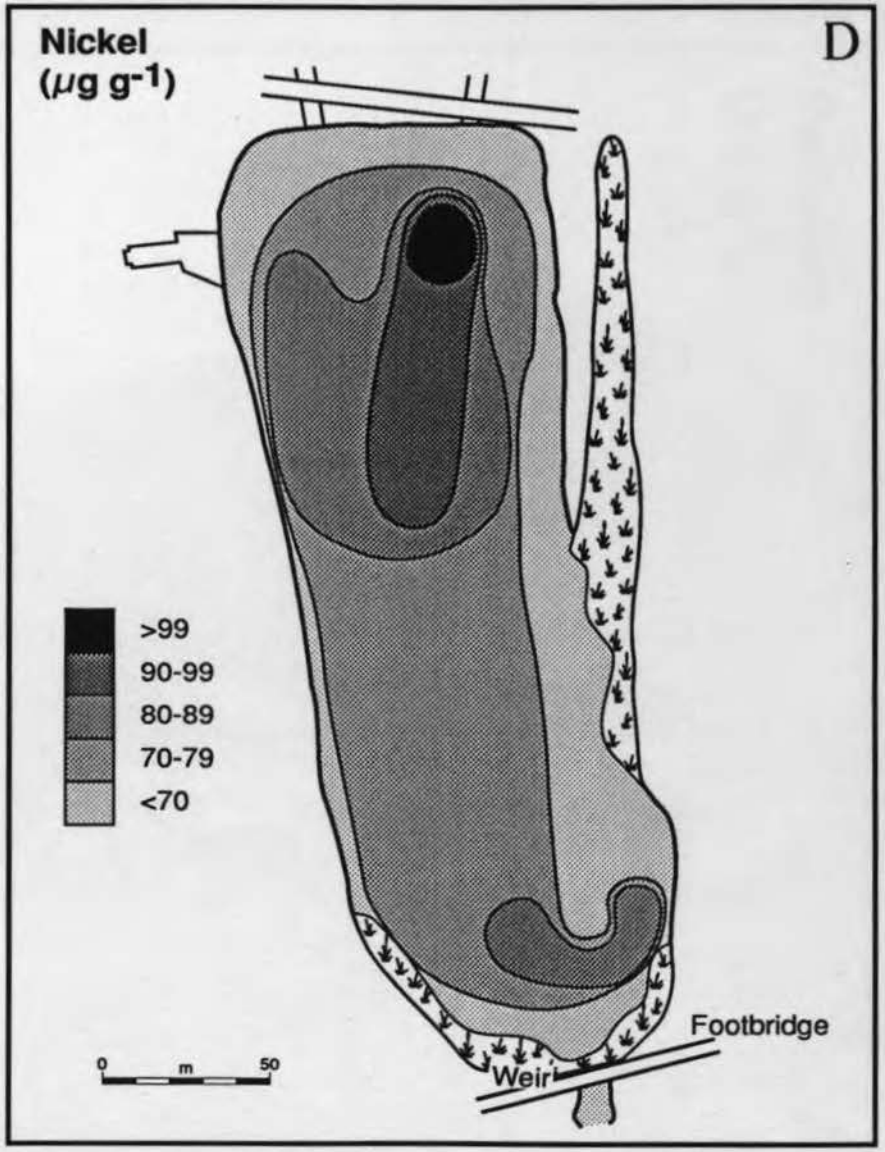
b. The spatial distribution of heavy metals in the top 1 cm sediments of the Pool

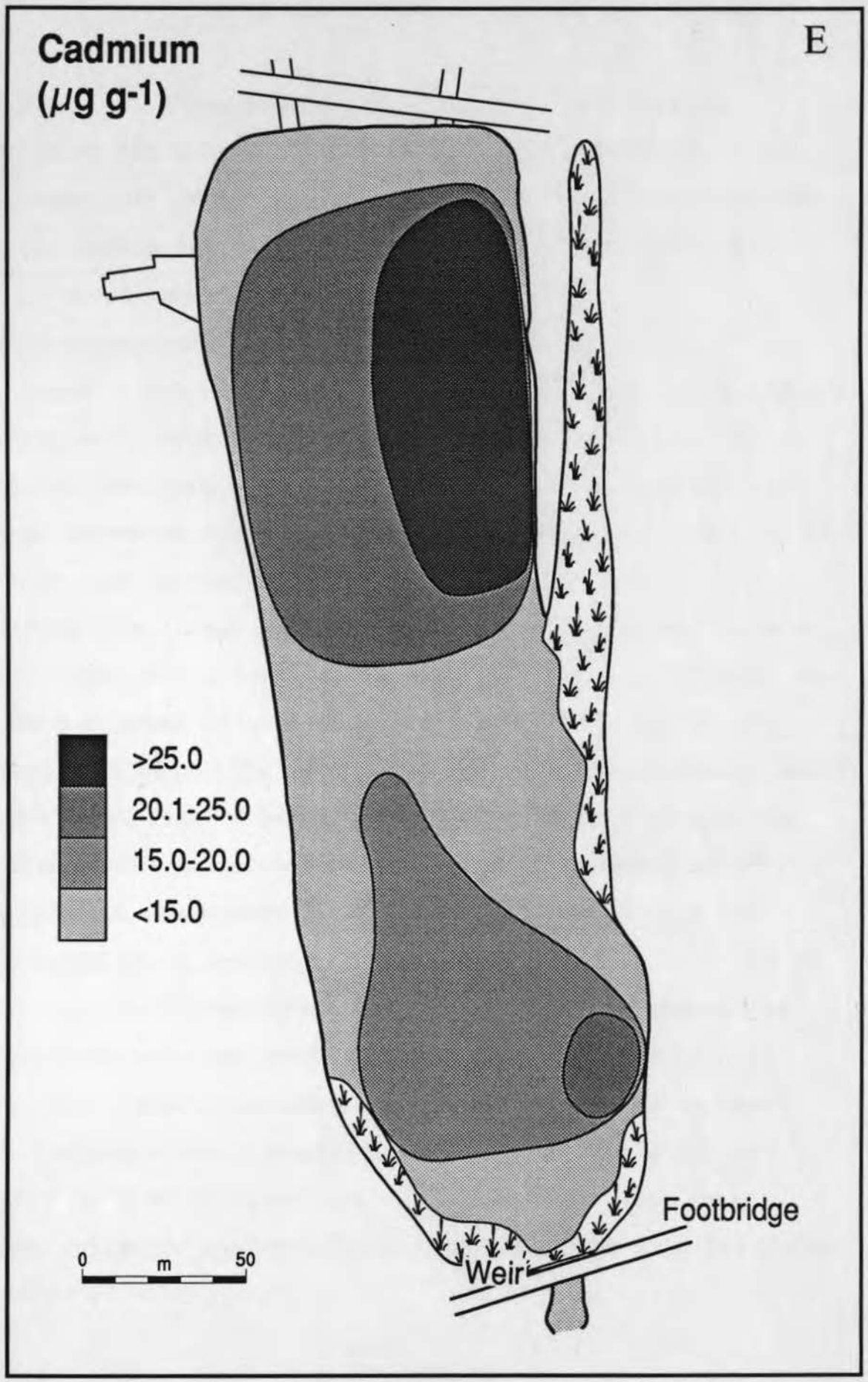
The spatial distribution of heavy metal concentrations in the top 1 cm sample of each core at Wyken Pool are presented in Figs 5.10 a-e. All metals show an area of high concentration immediately downstream of the eastern inlet and all except copper show a second area of high concentration around core DO, near the outlet. The area for the higher concentrations near the inlet becomes elongated towards the western shore in the cases of Cu, Ni and Pb and, in the cases of Zn and Cd, directly south towards the inlet. The area of high

Fig 5.10 Spatial distribution of heavy metals in surface lake sediments
a. Cu
b. Pb
c. Zn
d. Ni
e. Cd




Zinc
(μg g-1)
C
>1400
1000-1400
<1000
0
m
50
Weir
Footbridge


Nickel
(μg g-1)
D
>99
90-99
80-89
70-79
<70
0
m
50
Weir
Footbridge


Cadmium
(μg g-1)
E
>25.0
20.1-25.0
15.0-20.0
<15.0
0
m
50
Footbridge
Weir

concentration in the south, in all cases except Zn, is confined to the D transect; that of Zn covers both the C and the D transects. With the exception of Pb, the concentrations of heavy metals in the sediments near the inlets are higher than in those located near the outlet.

The concentrations of Cu vary from 121.31 $\mu g\ g^{-1}$ downstream of the eastern inlet to 43 $\mu g\ g^{-1}$ just below the junction with the area of marsh on the C transect. Values of Cu tend to decrease towards the outlet and also towards the eastern margin of the lake, more particularly near the junction with the marsh area. Apart from the high concentrations in the north, and the three low values on the eastern side of the lake, other values do not vary greatly.

The two areas of high Pb concentrations lie in the southeastern corner (761.2 $\mu g\ g^{-1}$) and to the north below the eastern inlet (494 to 481.5 $\mu g\ g^{-1}$). Concentrations tend to decrease to the south, with the lowest value (128.5 $\mu g\ g^{-1}$) obtained from the sample just below the junction with the marsh along the C transect on the eastern shore.

Values for Zn vary from 1428.6 $\mu g\ g^{-1}$ in the area above the junction with the marsh to 852.1 $\mu g\ g^{-1}$ on the western shore. The highest concentrations appear along the eastern shore sampled along transect 1, although the whole of the northern half of the lake has values exceeding 1000 $\mu g\ g^{-1}$, and two thirds of the Zn values in the southern half lie below 860 $\mu g\ g^{-1}$.

Concentrations of Ni decrease southwards and eastwards with a maximum of 107.6 $\mu g\ g^{-1}$ in the area immediately south of the eastern inlet. Concentrations decline to between 67.1 $\mu g\ g^{-1}$ and 65.5 $\mu g\ g^{-1}$ at the junction with the marsh on the eastern end of the C transect. There is an area of slightly higher Ni concentrations near the outlet, above 88 $\mu g\ g^{-1}$, but this is not marked when compared with the remaining values which are not below 77.9 $\mu g\ g^{-1}$.

Cd values do not vary greatly over the surface sediment samples of the lake. The highest values, above 25 $\mu g\ g^{-1}$, are found in the northern half of the lake, reducing to below 13 $\mu g\ g^{-1}$ in the southeast with a secondary area of slightly higher values in the area adjacent to the outlet (above 20 $\mu g\ g^{-1}$).

The highest values of heavy metals in Wyken Pool are on the eastern side of the Pool with 2 areas to the north and south of particularly high values. Sediment focusing may be responsible in part for the distribution of metals in the surface sediments, reflecting differential settling of coarse particles near the inflows and of finer particles near the outflow.

2. P, Fe and Mn content of lake sediments

This section is divided into two subsections to present the results of the distribution of P, Fe and Mn with depth in the

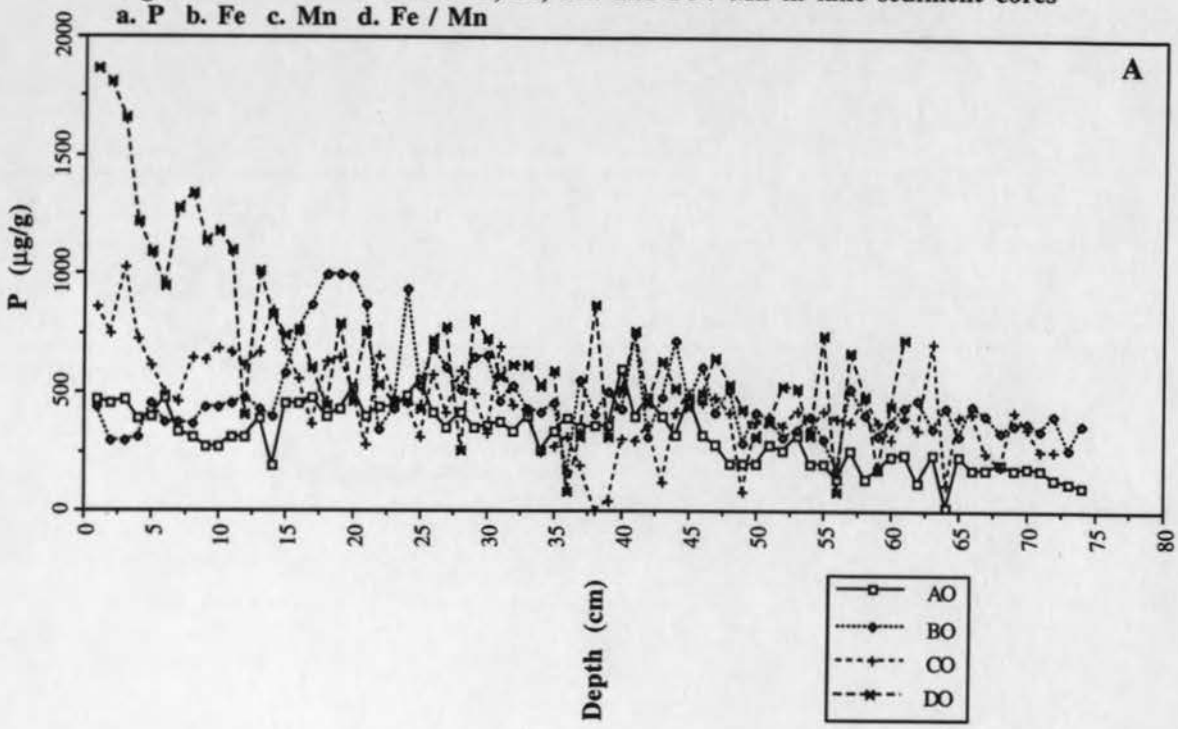
lake sediment cores, and also spatially in the surface samples of the lake.

a. Downcore trends in P, Fe and Mn content

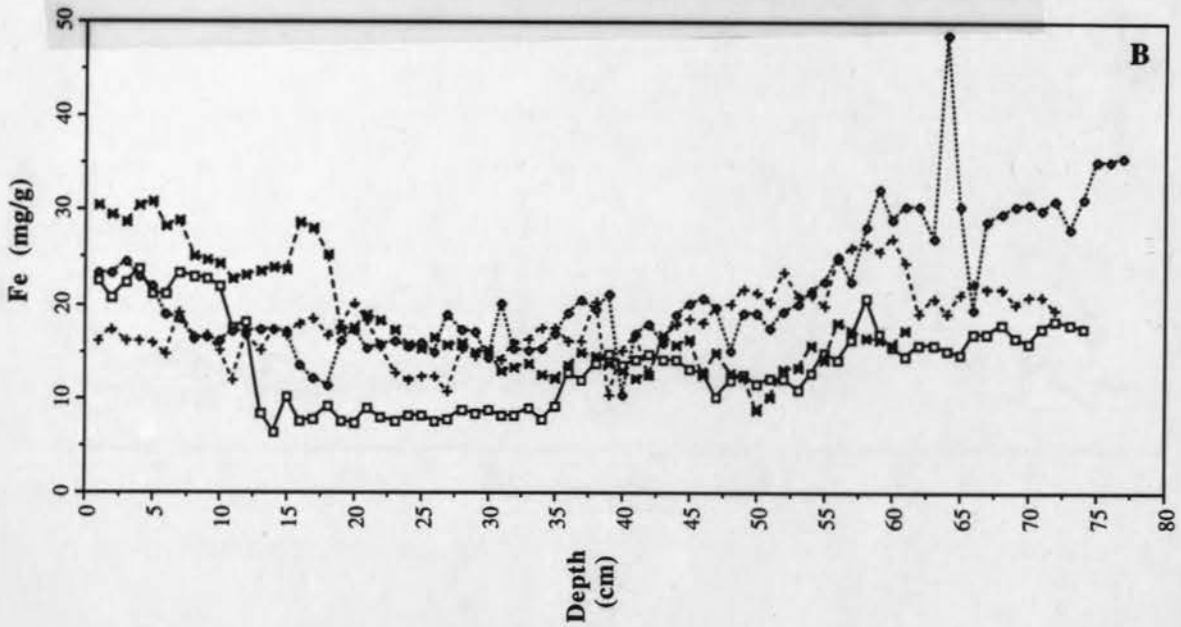
P concentrations in the lake sediment cores generally decrease with depth; the steepest decline occuring in the top 20 cm of the sediment core (Fig 5.11 a). The highest concentrations in the uppermost sediments were found in core D, nearest the outlet; the top sample of which exceeded 1800 $\mu g\ g^{-1}$. Cores A and B, nearest the inlets, contain the lowest concentrations of P, at 450 $\mu g\ g^{-1}$. The general trend of decreasing P concentration with depth below 23 cm is similar in all the cores. The decline is not smooth since there are considerable variations in each core towards the basal sediments. Basal samples range in P content from between 10 and 250 $\mu g\ g^{-1}$ in the longer cores, A, B and C, whilst core D reaches 750 $\mu g\ g^{-1}$ at its base.

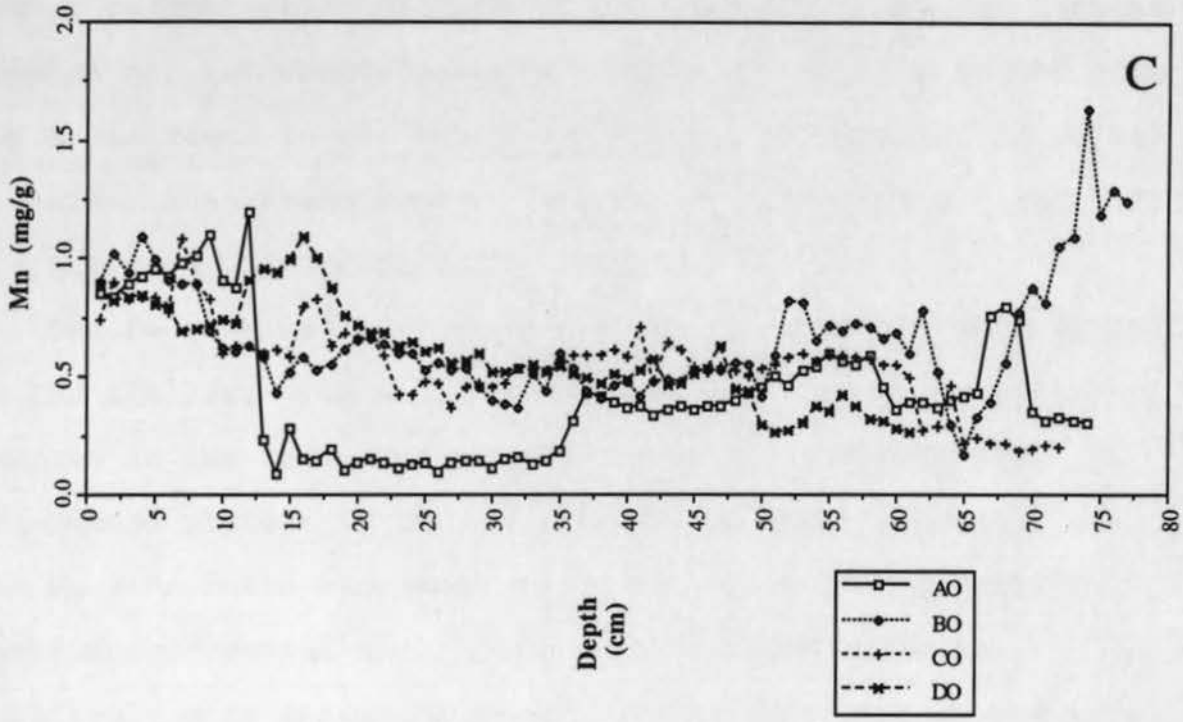
The profiles for Fe and Mn (Figure 5.11 b and c) are similar in outline to the heavy metals as the concentrations of each decreases with depth in the upper third of the core, decline to a central plateau and then rise again towards the base of the core. The central plateau is most pronounced in core A, where Fe concentrations decrease to approximately 8 mg g^{-1} and Mn to about 0.17 mg g^{-1}. The highest values are attained in the basal samples of core B where a single peak in Fe rises to 50 mg g^{-1} at a depth of 64 cm. The highest

Fig 5.11 Downcore trends in P, Fe, Mn and Fe / Mn in lake sediment cores
a. P b. Fe c. Mn d. Fe / Mn

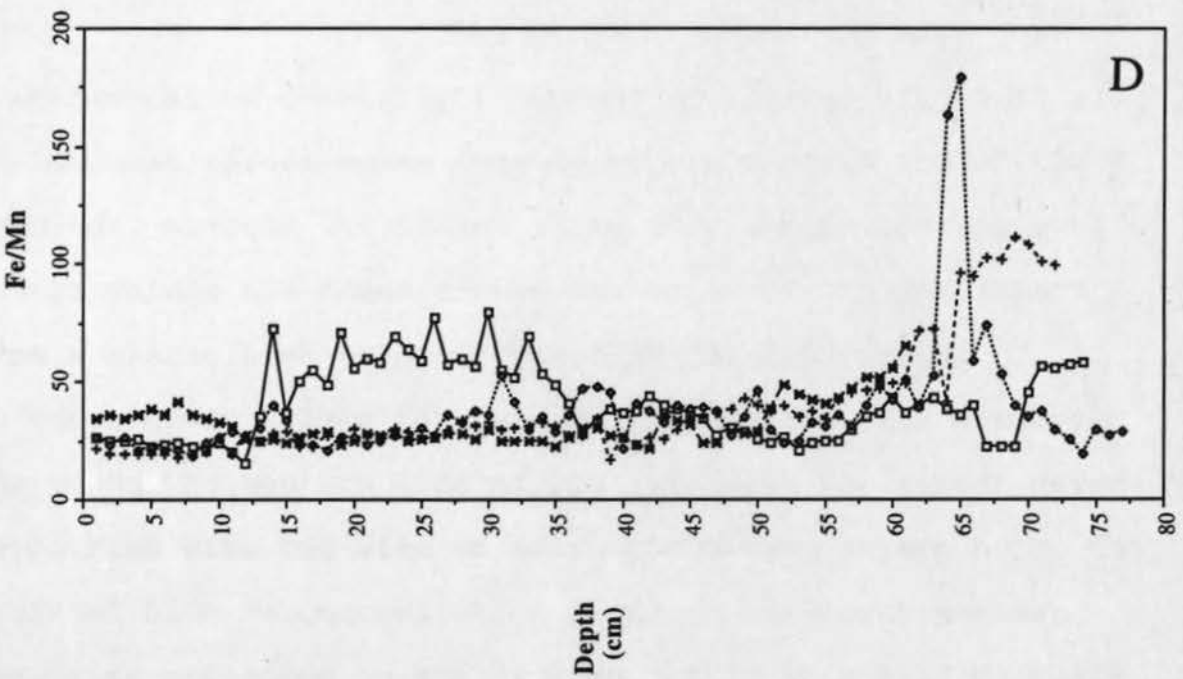


Depth of former soil surface
AO = 61 cm, BO = 65 cm, CO = 61 cm, DO = 51 cm





Depth of former soil surface
AO = 61 cm, BO = 65 cm, CO = 61 cm, DO = 51 cm



concentration of Mn is found at a depth of 74 cm in core B with a concentration of 1.65 mg g^{-1}. The values in the topmost samples are intermediate between those at the base of the core and those found in the central plateau. The range of Fe values are wider than those for Mn, between 16 and 30 mg g^{-1} and 0.75 and 0.9 mg g^{-1} respectively.

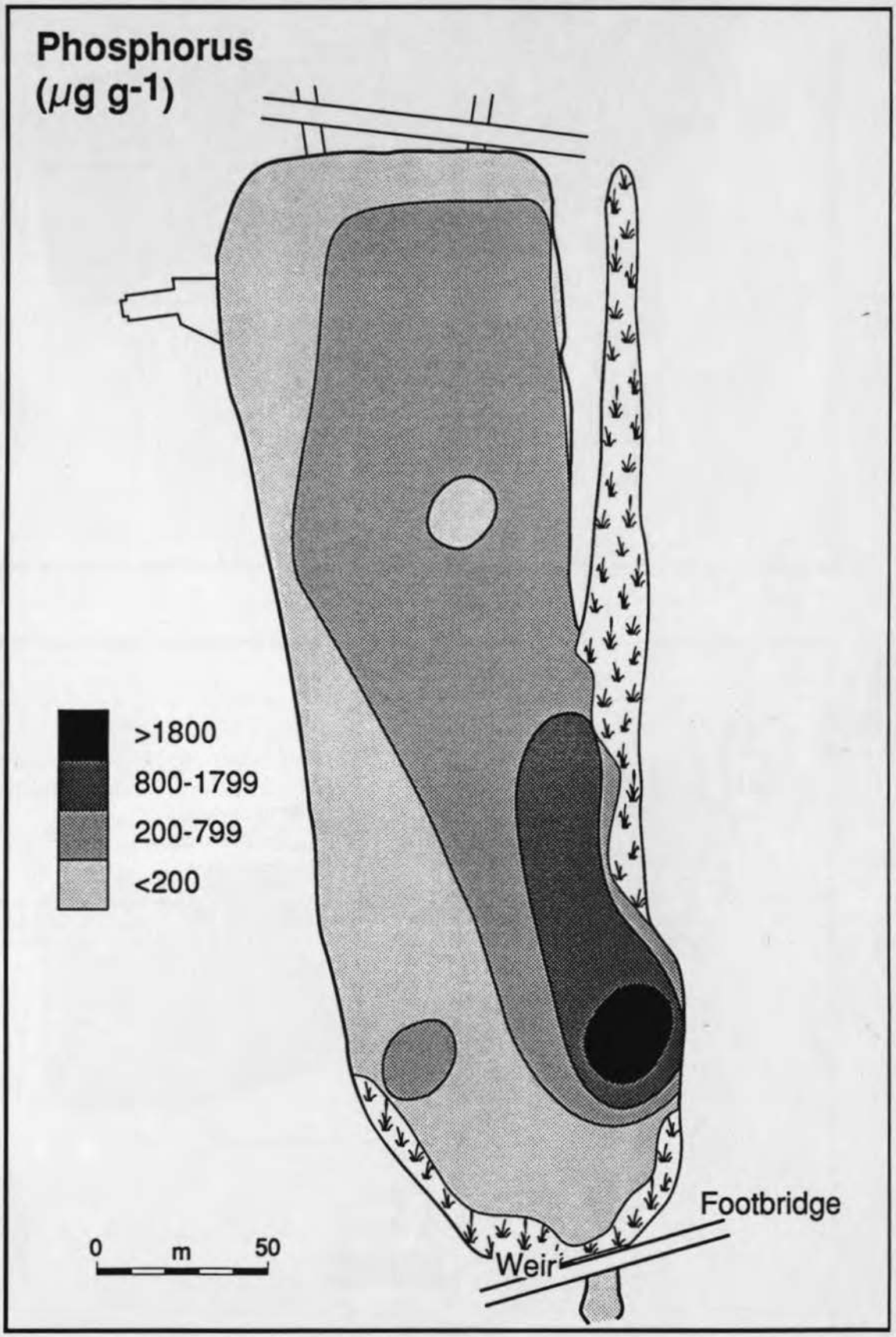
The Fe / Mn ratio (Figure 5.11 d) for all the cores except AO are similar, with a gradual increase in values to the basal samples in the core. The trace for core AO reflects the pronounced plateau in values between 13 and 36 cm depth, as the Fe / Mn ratio increases up to 80, reflecting generally lower Mn concentrations. Higher ratios could indicate relatively more oxidising conditions in this part of the core.

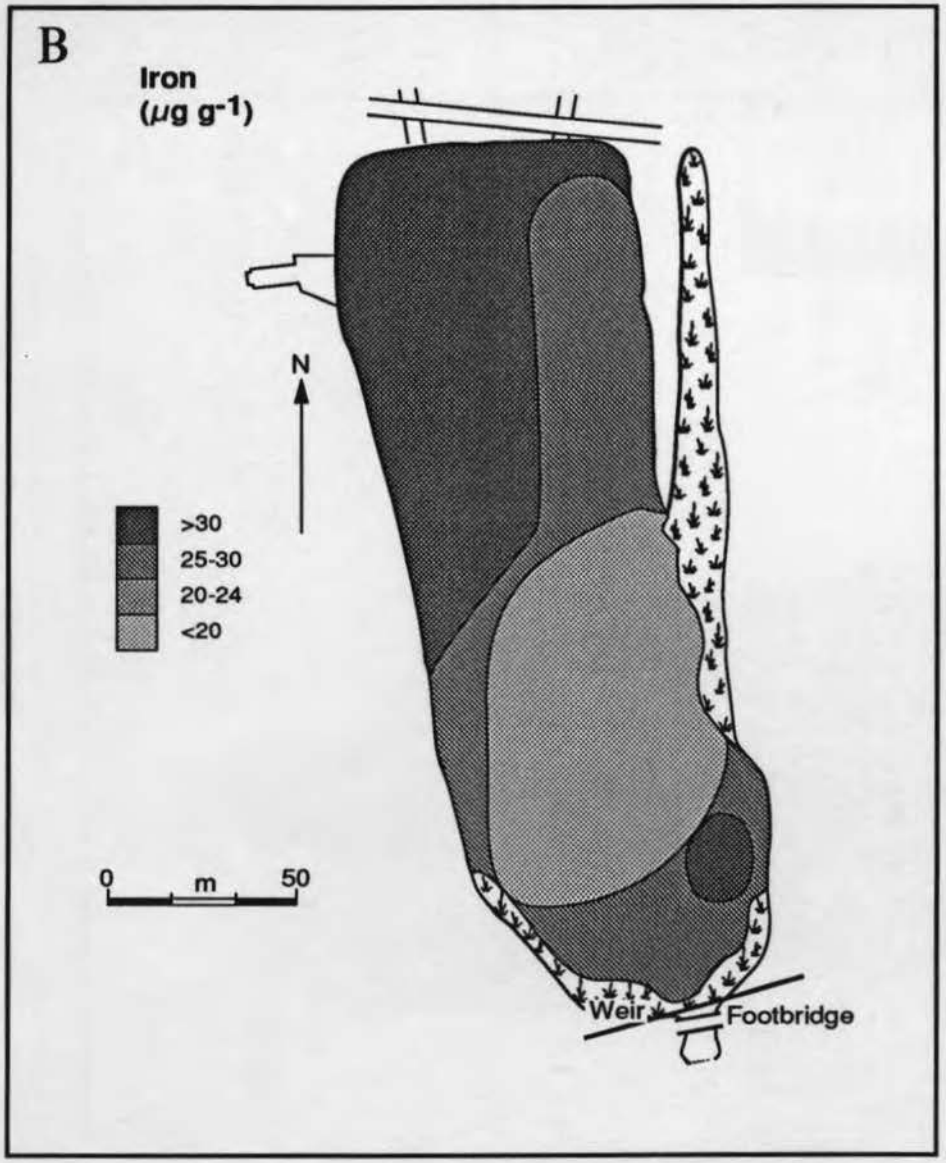
b. Spatial distribution of P, Fe and Mn in the surface samples of Wyken Pool

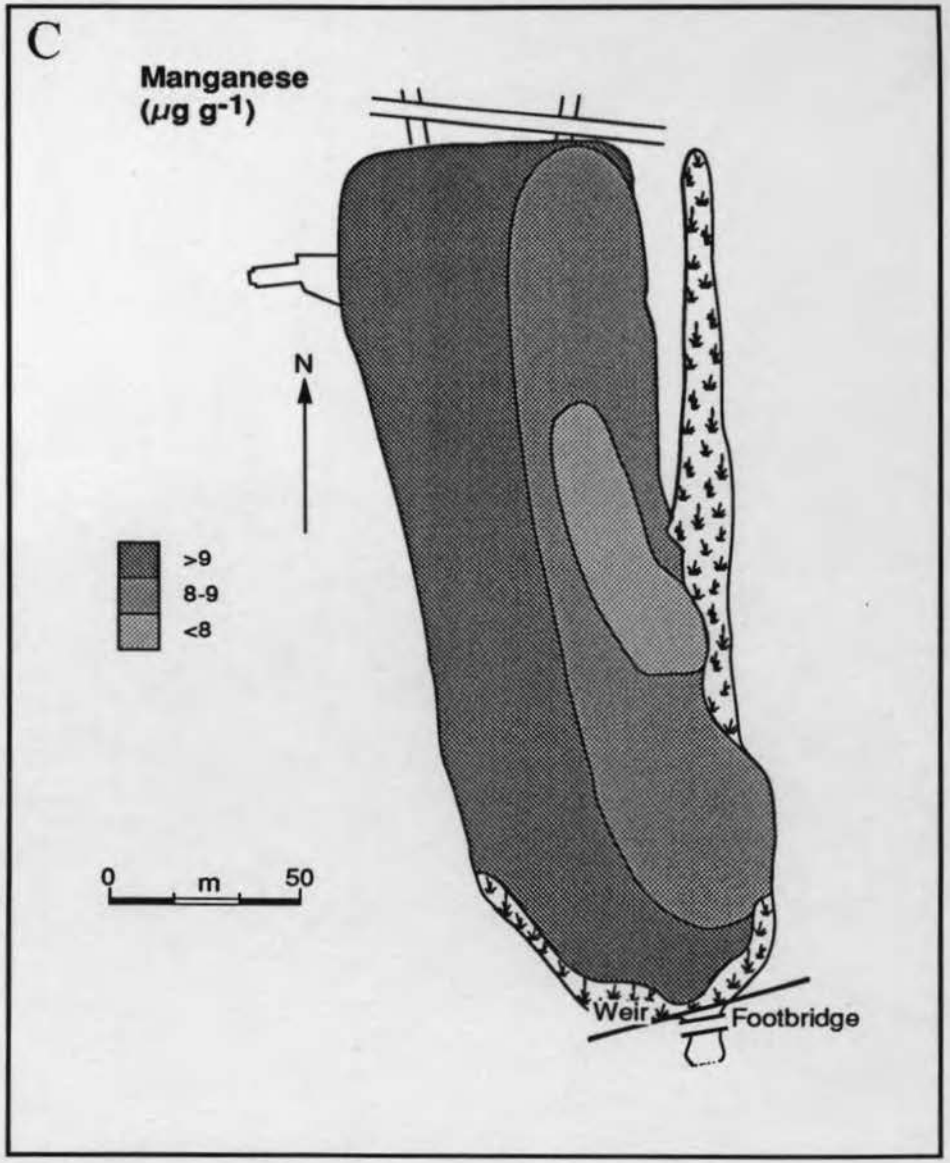
P concentration generally increases southwards (Fig 5.12 a), the highest values being located at the eastern end of the D transect, nearest the outlet where they exceed 1800 $\mu g\ g^{-1}$. Lowest values are found around the edges of the lake apart from a single high value in the southeastern corner.

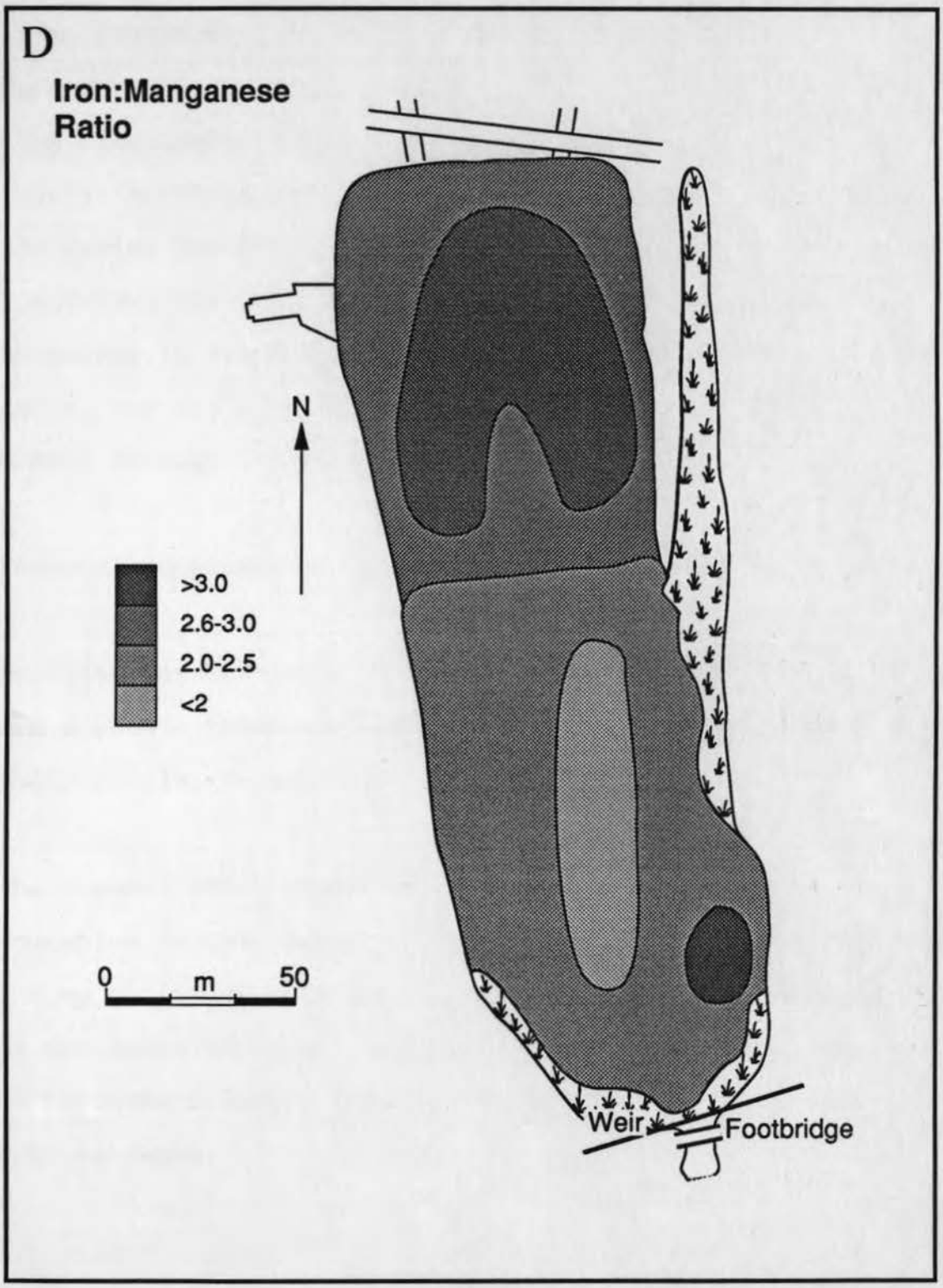
The highest values for both Fe and Mn (Fig 5.12 b and c) are along the western side of the lake with the lowest values associated with the area of marsh along the eastern bank. The isolated high Fe concentration found in the south eastern corner is reflected in the Fe / Mn ratio (Fig 5.12 d) where

Fig 5.12 Spatial distribution of P, Fe, Mn and Fe / Mn in the surface sediments of Wyken Pool
a. P
b. Fe
c. Mn
d. Fe / Mn




B
Iron
(μg g-1)
N
>30
25-30
20-24
<20
0
m
50
Weir
Footbridge


C
Manganese
(μg g-1)
N
>9
8-9
<8
0
m
50
Weir
Footbridge


D
Iron:Manganese
Ratio
N
>3.0
2.6-3.0
2.0-2.5
<2
0
m
50
Weir
Footbridge

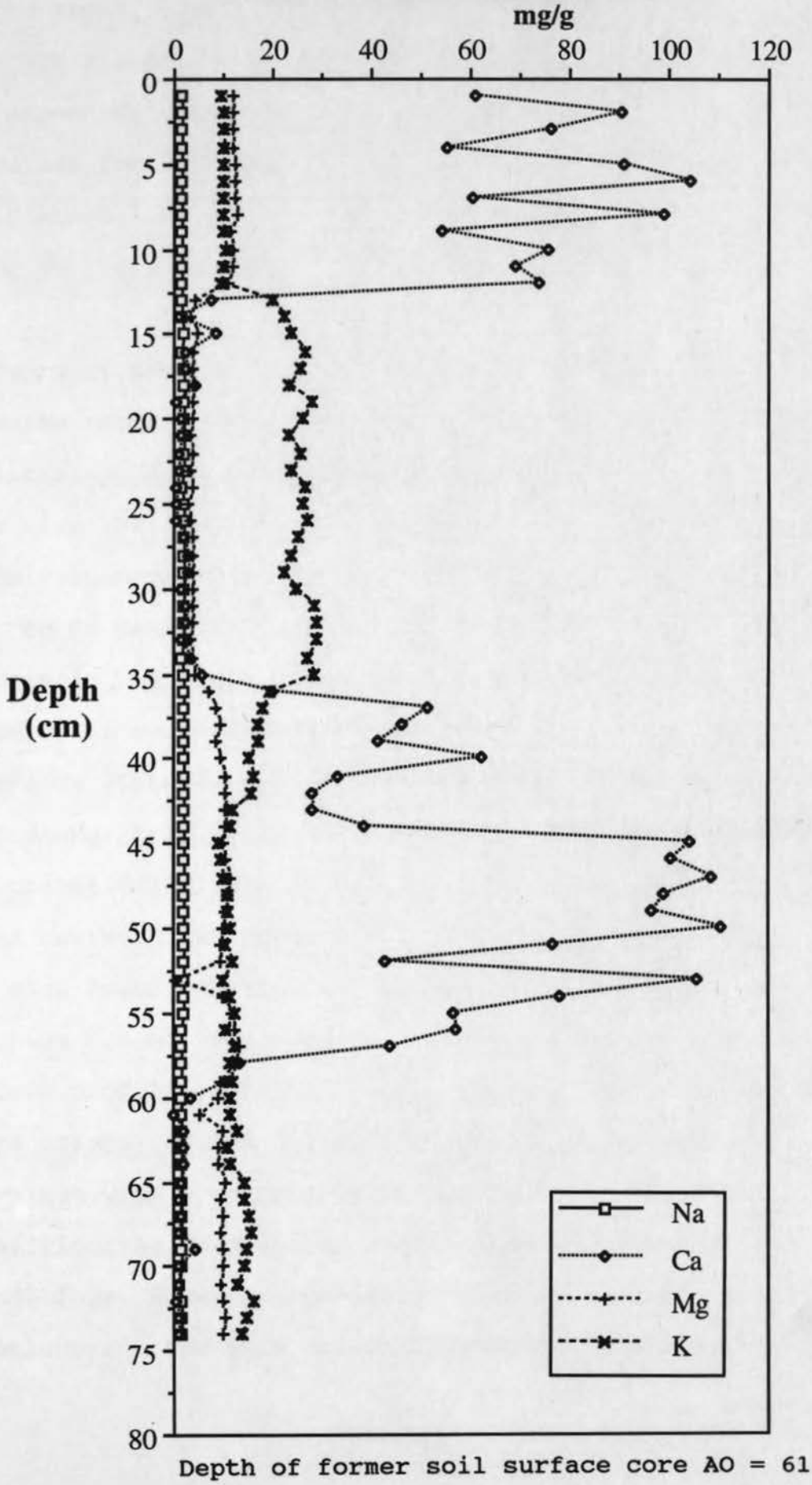
there is also a high value. The distribution of Fe / Mn ratio effectively divides the lake into two with the higher values mainly found to the north and lower values in the southern half. The lowest Fe / Mn ratio is found in the central southern part of the lake, perhaps reflecting relatively more reducing conditions. The highest Fe / Mn values are found in the central northern part of the lake representing relatively more oxidising conditions. This may be associated with aerated water entering the lake through the inlets. A second area of higher values is found along the D transect to the south of the marsh, and may also be associated with the influx of freshwater through the marsh.

3. Non-metallic elements

The profiles for total Ca, Mg and K concentrations (Fig 5.13) in core A show a threefold pattern similar to that shown by the heavy metals, Fe and Mn:

1. The element which shows the greatest variability in concentration in the upper 12 cm is Ca which ranges from less than 15 mg g^{-1} to over 25 mg g^{-1}. Average concentrations of K and Mg are about 10 mg g^{-1} and 12 mg g^{-1} respectively. Values for Na increase slightly from 1.5 mg g^{-1} to 1.65 mg g^{-1} at about 17 cm depth.

Fig 5.13 Downcore trends in Na, Mg, Ca and K content of lake sediment cores



2. At 13 cm depth, the concentrations of Ca and Mg fall to near zero and 3.5 mg g^{-1} respectively. This fall is mirrored by a corresponding rise in the concentration of K to nearly 30 mg g^{-1}. Values for Na remain constant from 17 to 56 cm with an average of about 1.75 mg g^{-1}, although a peak at 51 cm of above 2 mg g^{-1} is recorded.

3. At a depth of between 35 and 40 cm, Mg concentrations rise to just below those of the uppermost sediments. The values for K fall initially below those of the upper sediments, but then gradually rise to 14 mg g^{-1}. At 35 cm, Ca concentrations begin to rise to values which exceed those of the upper sediments. At 56 cm the Ca peak declines and values approach the limits of detection in the lower 11 cm of the core. Values for Na decline below 51 cm to an average of 1.35 mg g^{-1}.

The trends downcore for the non-metallic elements seem to suggest a change from 13 to 36 cm depth in all elements except Na. This change could be a reflection of changing sediment source and regime. This three-fold division of the downcore trend is also found particularly in core A0 in dry bulk density (Figs 5.6 a), and also to a certain extent in the heavy metals profiles. Whilst P and organic matter do not show a mid-core change, Fe and Mn, particularly core AO, show lowered values with a corresponding rise in Fe / Mn ratio which traditionally (Mackereth, 1966) suggested a change in redox conditions. However, changes in the non-metallic metal concentrations and the bulk density parameters suggest that

the Fe and Mn may, in fact, reflect a change in sedimentation rather than changing redox in this case.

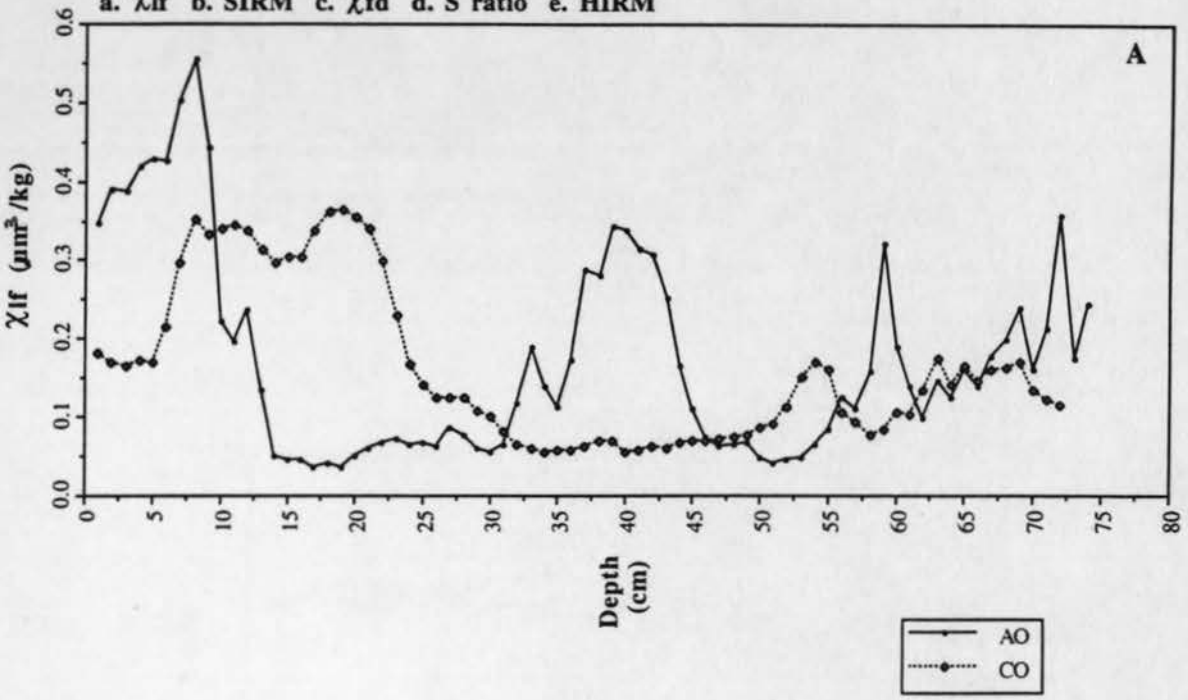
5.2.5 Mineral magnetic properties of the lake sediments

As discussed in Chapter 4.2.5, mineral magnetic measurements were carried out for three main reasons (Chapter 2.10 ie) for the purpose of tracing pollution history. These were: correlation of a grid of cores, tracing the sources of sediment to the lake and the use of magnetic measurements as a surrogate for heavy metals analysis. The latter will be addressed in section 5.3 iii, but the rest of this section will be divided into three subsections. The first section will describe the results obtained. This will be followed by an examination of a grid of SIRM and χ_{lf} profiles which attempt to establish synchronous horizons across the lake and hence correlate the suite of cores. Lastly, mineral magnetic characteristics will be used to resolve the changing nature of the sediments through time.

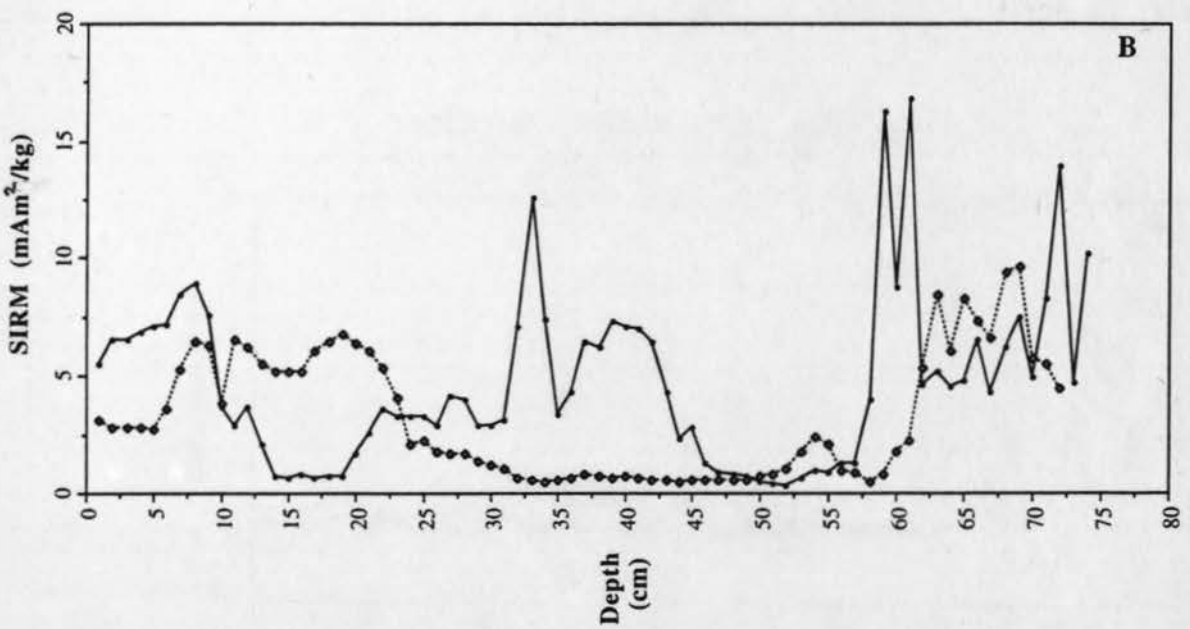
a. Mineral magnetic characteristics of the lake sediments

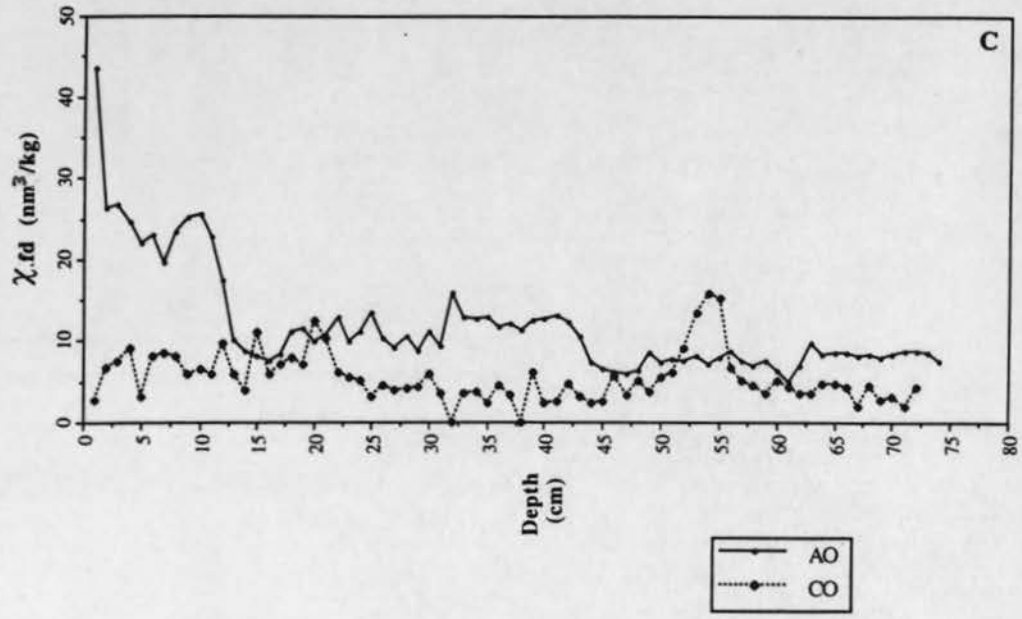
Figs 5.14 a and b show profiles for χ_{lf} and SIRM respectively from cores AO and CO. The highest values for χ_{lf} in both cores are found in the top 13 (AO) and 21 samples (CO), where χ_{lf} reaches 0.57 $\mu m^3\ kg^{-1}$ and 0.36 $\mu m^3\ kg^{-1}$ in AO and CO respectively. Beneath these high values in each core is a

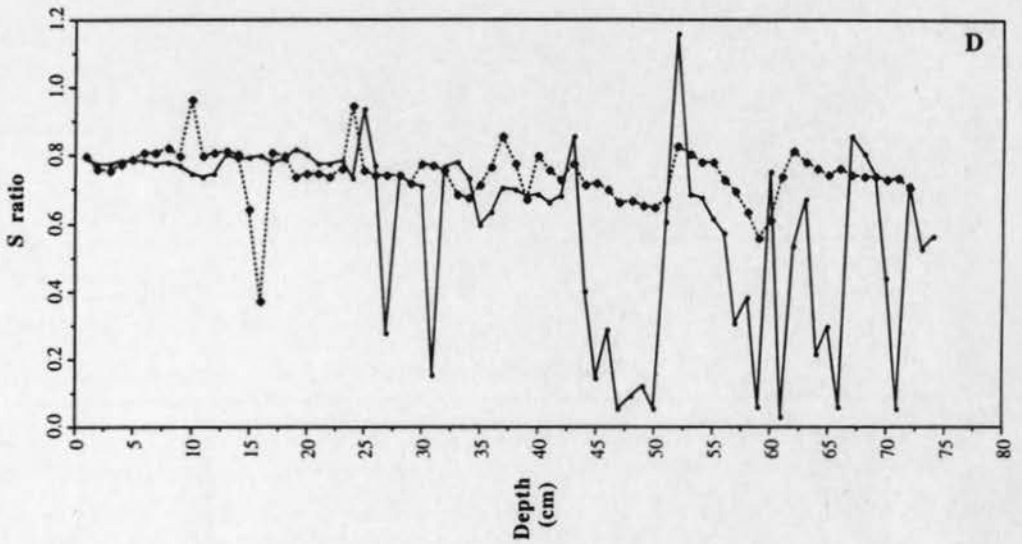
Fig 5.14 Mineral magnetic properties of core AO and BO
a. χlf b. SIRM c. χfd d. S ratio e. HIRM



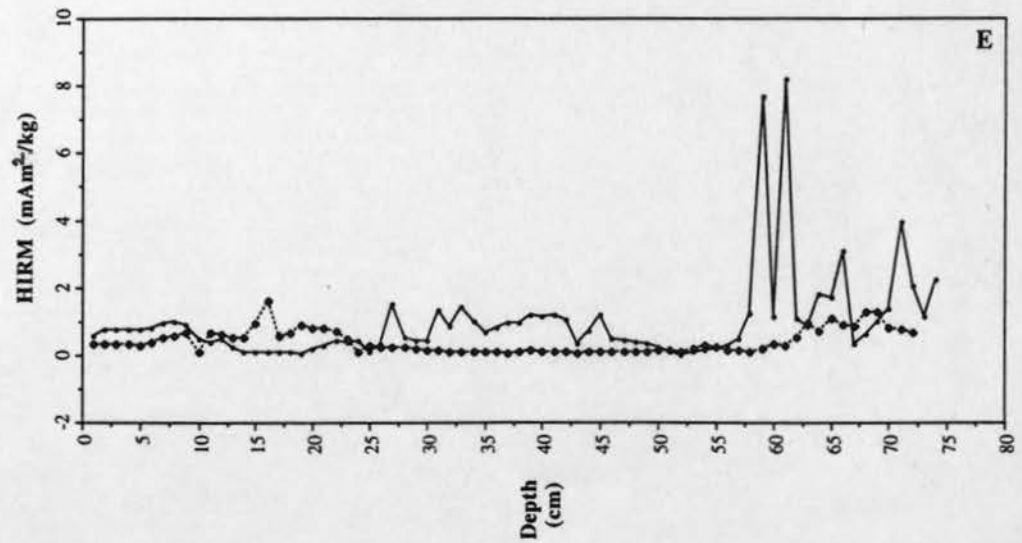
Depth of former soil surface
AO = 61 cm, CO = 61 cm,







Depth of former soil surface
AO = 61 cm, CO = 61 cm



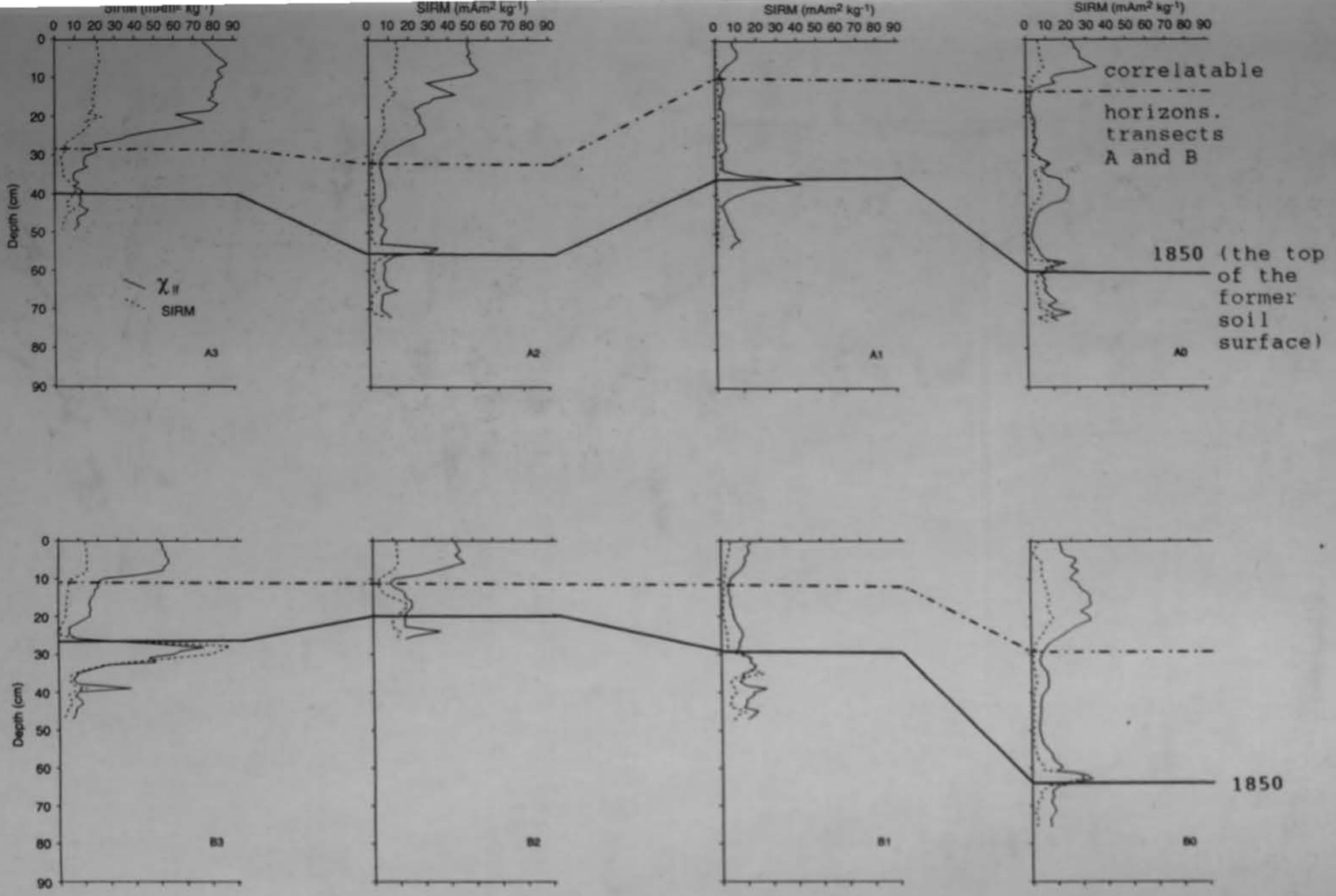
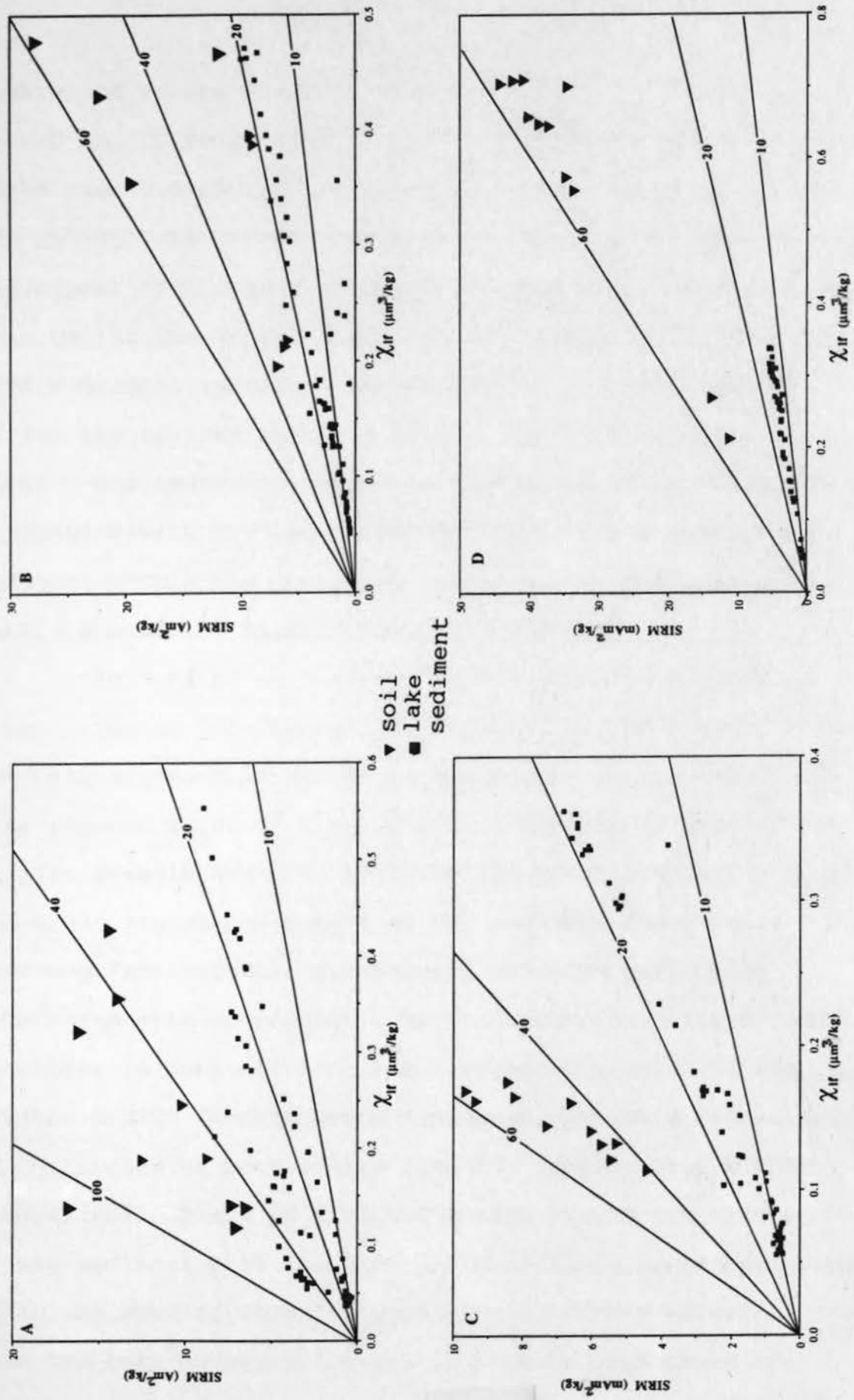


Fig 5.14 f Matrix of χ_{lf} and SIRM for all lake cores

Fig 5.14 g Scattergrams of χ_{lf} against SIRM for lake sediment cores

a. AO b. BO c. CO d. DO



trough where values are less than 0.1 and 0.05 $\mu m^3\ kg^{-1}$ in cores AO and CO respectively. This trough is followed by a peak to over 0.3 $\mu m^3\ kg^{-1}$ in core AO at a depth of 40 cm and 0.175 $\mu m^3\ kg^{-1}$ at a depth of 54 cm in core CO. Values decrease until a peak at the junction with the soil at a depth of about 60 cm. Whilst the values fluctuate within the soil, the trend is for a gradual increase down to the basal samples. SIRM profiles are similar to those of χ_{lf} with high values in the uppermost sediments, a central peak at about 35 cm depth and the junction with the soil indicated by a marked peak. SIRM fluctuates within the soil, but there is a general trend of slightly increasing values with depth.

χ_{fd} (Fig 5.14 c) values for core CO fluctuate around 5 $nm^3\ kg^{-1}$. Values for core AO are slightly higher than CO with an average of about 10 $nm^3\ kg^{-1}$, and higher values are found in the topmost 12 cm of core AO with a maximum of over 40 $nm^3\ kg^{-1}$. The S-ratio and HIRM profiles are presented in Fig 5.14 d and e and are mirror images of one another. The S-ratio reflecting ferrimagnetic mineralogy, and HIRM reflecting antiferromagnetic mineralogy. The trace for the S-ratio shows high values in both of the cores (between 0.8 and 0.7) and indicates a high ferrimagnetic component, possibly magnetite. Core AO fluctuates more widely than CO, particularly within the basal soil. There is a marked trough at the junction of the lake sediment with the underlying soil, followed by a peak and, in the case of core CO, gradually declining values. Within the lake sediment, values of HIRM in both cores are

low. Samples from core CO do not exceed 1 $mAm^2\ kg^{-1}$ and the maximum for AO is just over 1 $mAm^2\ kg^{-1}$. However, at the junction of the lake sediment with the basal soil in both cores there is a peak which is more pronounced in core AO; reaching over 8 $mAm^2\ kg^{-1}$, and exceeding 3 $mAm^2\ kg^{-1}$ in core CO. Values within the soil are variable and a trend cannot be identified. The reasonably steady values for both the S-ratio and HIRM in both of the cores indicates that the source of magnetic minerals to the sediment deposited in the lake has changed little since the basin subsided.

b. χ_{lf} and SIRM profiles for core correlation

A matrix to show magnetic profiles throughout the grid of lake cores was compiled using χ_{lf} and SIRM. This is presented in Fig 5.14 g.

In general, the χ_{lf} profiles of the lake sediment can be divided into two areas :

1. The upper samples show fluctuations in comparison with the sediments below. At depths ranging from 5 to 10 cm the area of fluctuation is terminated in most cases by a peak. Values are higher in these upper sediments than in the ones below. The point at which values decrease provides a point of synchronous correlation in some cores. However, the higher values are not found across the whole suite of cores and, particularly in the southern half of the grid, is hardly present at all. This

feature does not, therefore, provide a lake-wide correlatable horizon.

2. Below this peak in the core is a zone of decreasing χ_{lf} with little fluctuation about the mean; again terminated by a peak at the boundary with the buried soil. This peak enables closer definition of the boundary between the gyttja and the soil than would be possible by the use of visual stratigraphy alone.

In general the trends shown by SIRM are similar to those of χ_{lf}, although the curves themselves tend to exhibit less variability. Mineral magnetic measurements provided better resolution of the boundary between the gyttja and the buried soil than visual stratigraphy, but did not provide a suite of time-synchronous horizons with which to correlate the grid of cores across the lake.

c. Mineral magnetic characteristics as an indicator of changing sediment source with time.

In subsection a.), it was suggested from measurement of the S-ratio and HIRM that the concentration of the magnetic minerals in the lake sediment had changed little. A change in sedimentation rate is suggested by much of the analysis as exemplified by the three zones in the downcore profiles of not only χ_{lf} and SIRM, but also bulk density and, to a lesser

extent, heavy metal concentrations. This could relate to construction within the catchment leading to erosion of non-contaminated soils and dilution of the signal. Wolman (1967) showed that sediment delivery increased during the construction stage of urbanisation, but then returned to approximately its pre-urbanisation level once construction ceased. Douglas (1985) and Brookes (1988) suggest that after the construction phase, and with increasing channelisation, sediment delivery can actually decrease below levels expected by natural stream channels. Grew (1990) found that concentration profiles of heavy metals in Seeswood Pool decreased sharply post-1960 due to increased sediment yields from non-enriched bank sediments. This lead to dilution of the contaminated sediments and hence a decrease in concentration. The documentary history of Wyken Pool (Chapter 3.4.2) indicated that there were two major phases of construction in the catchment and one major disturbance. These were:

1. Construction of residential housing in the 1950s and 60s to the north of Wyken Pool in the Longford area.

2. Industrial and road construction in the 1960s and 70s with the building of the Bayton Road Industrial Estate and the M6 motorway.

3. The improvement of drainage through the marsh in the 1970s.

The latter would also have encouraged further sediment delivery to the lake, not only by the process itself, but also by providing unimpeded flow from contaminated areas of the catchment to the lake. The possible disturbance of sediment delivery to Wyken Pool will be considered in detail in Chapter 6.

To specifically apply mineral magnetic measurements to assess whether the magnetic mineral source has changed with time, scattergrams of χ_{lf} against SIRM were used. These were also used for Swanswell Pool (Chapter 4.2.5c) and Fig 4.16 illustrated the theory behind their use.

Scattergrams of χ_{lf} against SIRM for lake sediment cores from each of the east-west transects are shown in Fig 5.14 g. Two distinct trends are apparent on each plot; a high SIRM/ high χ_{lf} trend corresponding to the soil at the bottom of each core and a high χ_{lf}, lower SIRM trend representing the lake sediment. Superimposed on these scattergrams are lines of gradient representing ratios of 10:1, 20:1, 40:1, 60:1, 80:1 and 100:1. The lake sediments all lie between the 10 and 20 ratio lines indicating that they are dominated by MD magnetite or particulate bound pollutants. Decreasing ratios indicate an increasingly ferrimagnetic mineralogy, such as magnetite, and increasing magnetic grain size. Increasing ratios indicate an increasing canted antiferromagnetic component, such as haematite. The soils either lie between ratios of 40 and 60 (cores CO and DO) or between 60 and 100 (AO and BO) which indicates that they could be dominated by SD grains such as

21

goethite. The lack of variability in the mineral magnetic properties of the lake sediments indicate that the source of magnetic minerals to the sediments probably has not changed over time.

Mineral magnetic measurements show the difference between the lake sediments and underlying soil and the dominance of pollution particles in the uppermost gyttja. Downcore profiles of mineral magnetic characteristics can be divided into three sections, as can other parameters, suggesting that whilst the source of the magnetic minerals in the sediment has probably not changed, the magnetic signal may have been diluted at some time in the past. Core correlation to provide a suite of time synchronous horizons across the whole lake was not possible.

Chapter 4.2.6 addressed the problem of whether the trends in magnetic mineral properties and heavy metals in Swanswell Pool reflected pollution histories, or complex sedimentation and sorting patterns within the lake. Variability of various properties of the lake sediments from Wyken Pool are presented in Table 5.8 and show that, as with Swanswell Pool, there is a possibility that mineral magnetic properties owe their distribution as much to the internal characteristics of the lake, as with trends through time. Trends in heavy metals, however, appeared to provide a reasonable representation of the history of pollution.

Table 5.8 Coefficient of Variation at 2 standard deviations (95%) for surface sediments and a lake sediment core from Wyken Pool. From Foster & Charlesworth (1994).

	Surface samples n=16	Core n=58
DBD	47.1	55.3
χ_{lf}	129.5	130.9
SIRM	140.9	170.8
IRM	135.0	178.6
S-ratio	10.5	24.3
HIRM	134.8	187.1
Pb	99.1	175.0
Cu	110.7	292.3
Ni	26.8	40.0
Zn	36.9	181.3
Fe	128.5	43.9
Mn	22.4	139.5

DBD = dry bulk density

5.2.6 Dating using ^{210}Pb and ^{137}Cs

In order to put the history of heavy metal pollution in Wyken Pool into an absolute timescale, one lake sediment core was subjected to radioisotope dating as outlined in Chapter 2.12. The results are presented in 2 subsections which will discuss ^{210}Pb and ^{137}Cs separately. Results of the analysis undertaken in the Physics department at Coventry University are presented in Table 5.9a and Fig 5.15.

i. ^{137}Cs

^{137}Cs activity is below the limits of detection of the instrument by 21 cm depth. The activity at 20 cm is low which strongly suggests that 20 to 21 cm depth in the sediment core may mark 1954 (Chapter 2.12) when nuclear testing began, giving an average accumulation rate in the last 39 years of 0.54 cm yr^{-1}. The peak in ^{137}Cs activity is found at a depth of around 15 cm which may represent 1963 and which is consistent with the average accumulation rate calculated from the possible 1954 horizon. Fig 5.15 shows a gradual increase in ^{137}Cs activity from 20 cm to 15 cm when there is a decline to under 10 mBq g^{-1}. Activities rise again at 5 - 6 cm depth, to fall to under 1 mBq g^{-1} at 4 cm depth. Above 4 cm, activities once again increase. The lower activities may represent the influx of channel bank material and the higher activities may represent topsoil sources (Foster & Walling, 1994). If this is the case, and assuming constant

Fig 5.15 Down core 137Cs activity in core C1 (mBq/g)

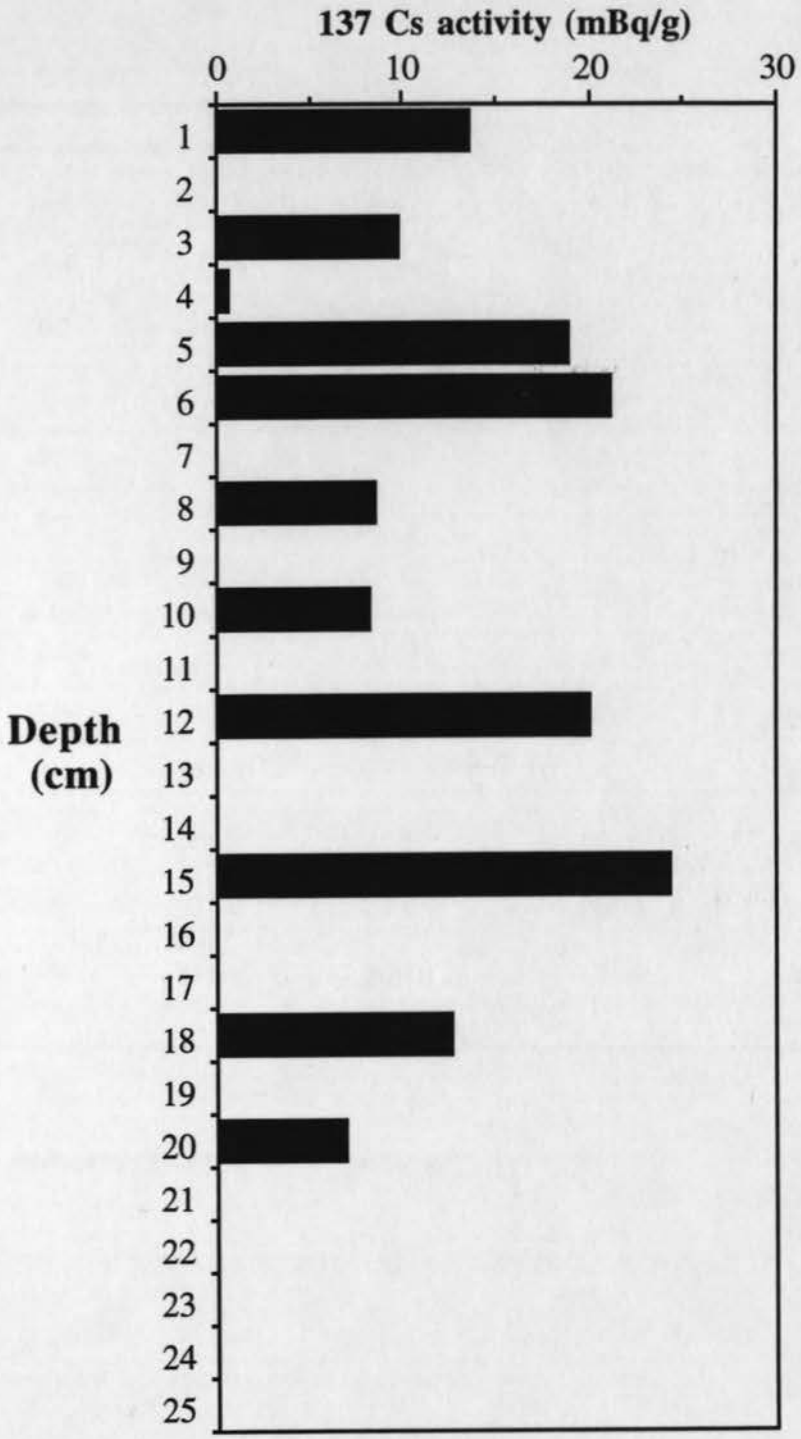


Table 5.9 a Activities of ^{210}Pb and ^{137}Cs in the sediments of core C1 at Wyken Pool (mBq g^{-1}).

Depth (cm)	^{137}Cs activity	% error	total ^{210}Pb	supported ^{210}Pb	unsupported ^{210}Pb	% error
2	13.6	40	50.8	9.0	41.8	36
3	9.74	42	56.8	5.1	51.7	26
4	0.6	60	50.1	0.0	50.1	16
5	19.0	21	41.9	3.2	38.7	14
6	21.2	23	61.7	0.0	41.9	40
8	8.5	40	39.4	0.0	39.4	26
10	8.2	55	28.8	12.5	16.3	99
12	20.0	24	0.0	7.9	0.0	00
15	24.3	15	0.0	8.7	0.0	00
18	12.7	21	13.3	6.0	7.1	80
20	7.0	31	27.8	7.7	20.2	50
21	0.0	00	0.0	0.0	0.0	00
25	0.0	00	0.0	0.0	0.0	00

0 indicates not detectable above background

sedimentation of 0.54 cm yr^{-1} (ie 39 yrs/ 20 cm), then the low values at 10 and 8 cm depth could cover the period from about 1972 - 1976, which may be related to channel bank erosion during a combination of the construction of the Bayton Road Industrial Estate in 1969, the building of the M6 motorway in 1971 and the improvement of drainage through the marsh in 1975 (Chapter 3.4.2). However, these interpretations are based on the incomplete measurement of one core, and this would need further corroboration using measurements from other cores before anything other than tentative conclusions can be drawn.

The soil surface, (dated at approximately 1850), is reached at 70 cm in core C1. The sediment between 20 cm and 70 cm represents that accumulated between 1850 and 1954, an average accumulation rate of 0.481 cm yr^{-1}. However, as sediments accumulate, they are compressed, the upper sediments having a lower bulk density than those lower down the core (Fig 5.6). Calculations carried out in order to correct for this found that the upper 20 cm would occupy 13.45 cm, some 6.55 cm less if they were the same density as sediments below. The accumulation rate for the sediments since 1954 can therefore be corrected to an average of 0.345 cm yr^{-1} using ^{137}Cs as a means of dating. This would suggest that the sediment accumulation rate is slightly lower in the more recent sediments and higher in those pre-1954.

ii. ^{210}Pb

Like Swanswell Pool, unsupported and supported ^{210}Pb are beyond the limits of detection by 20 cm depth. In comparison to Swanswell Pool, however, the ratio of unsupported : supported ^{210}Pb is fairly low in the upper sediments. Table 5.9 b compares ratios of surface activities from Wyken and Swanswell Pools as well as Merevale Lake and Seeswood Pool which were discussed in section 4.2.6 ii.

The supported component in Wyken Pool is about half the supported component in Swanswell Pool. The unsupported component in Wyken Pool is about 0.23 that of Swanswell Pool and the total ^{210}Pb activity in the top sample of Wyken Pool is 0.27 that of Swanswell Pool. Since the unsupported component is derived mainly from atmospheric sources (4.2.6 ii), then Table 5.9 illustrates that the atmosphere is not as important a source in Wyken Pool with 82% of the total ^{210}Pb being derived from unsupported sources. This leaves about 28% derived from catchment sources. The proportion derived from the atmosphere in Merevale Lake and Seeswood Pool is 76% and 51% respectively, which means that the unsupported component in Wyken Pool lies between the rural and city centre sites.

Table 5.9 b ^{210}Pb activities (mBq g^{-1}) from Wyken and Swanswell Pools compared with those from other Midland England lakes.

	1	2	3	4
a) Total	50.8	190.0	159.7	64.8
b) Supported	9.0	4.4	38.1	31.1
c) Unsupported	41.8	185.6	121.6	33.7
b:c	4.6	42.2	3.2	1.1
a:c	0.82	0.98	0.76	0.51

1 = Wyken Pool

2 = Swanswell Pool

3 = Merevale Lake

4 = Seeswood Pool

Unpublished data for sites 3 and 4 supplied by IDL Foster, Coventry University.

Calculating the annual deposition rate of ^{210}Pb at Wyken Pool, as outlined in section 4.2.6 ii, the dry bulk density for the top sample at Wyken Pool is 0.212 g cm^{-3} (Fig 5.6 a) and, if the accumulation rate calculated for the sediments from 1954 to the present day based on the ^{137}Cs date is used, the accumulation rate is 0.345 cm yr^{-1}. The annual deposition rate for Wyken Pool is therefore:

50.8 mBq g^{-1} (Table 5.9a) x 0.212 g cm^{-3} x 0.345 cm yr^{-1} =

3.72 mBq cm^{-2} yr^{-1}

In comparison with the range of values given by Oldfield & Appleby (1984), of between 12.95 and 20.35 mBq cm^{-2} yr^{-1}, the value for Wyken Pool is very low. As stated by Oldfield & Appleby (1984), there is no conclusive proof that there is a direct relationship between input and fallout, but they suggest it is a first test of the validity of the measurement. In the case of low values, Oldfield & Appleby (1984), suggest that the results may be poor, residence times may be low and sediment focusing may be a problem. Low trap efficiency may cause loss to outflow, problems with estimating trap efficiency in both lakes is discussed in Chapter 2.3 and is therefore not pursued further here. Eakins (1983), suggests that the catchment contribution to unsupported ^{210}Pb is probably the greatest uncertainty in using this radionuclide in dating. Four reasons were discussed in Chapter 4.2.6 ii for the lack of a complete profile in Swanswell Pool. Those of migration in the sediment column and problems with sediment resuspension and focusing are similar for Wyken Pool and so are not discussed further. Catchment disturbance and flux of unsupported ^{210}Pb to the lake sediments are discussed below:

1. The flux of ^{210}Pb should be constant but this cannot be guaranteed in urban lakes whose catchments are characterised

by disturbance. Chapter 3.4.2 outlined the construction that occurred in the catchment between 1950 and 1970 with the building of residential housing, the Bayton Road Industrial Estate, the M6 motorway and the draining of the marsh by the western inlet to the Pool. These appear to be reflected in the lake sediment cores, by increased bulk density in some profiles, especially the A transect near the inlets, heavy metal concentrations and mineral magnetic characteristics. It would appear, therefore that the flux of ^{210}Pb to the sediments at Wyken Pool, unlike that at Swanswell Pool, has not been constant through time.

2. The residence time of ^{210}Pb in the atmosphere should be constant. The calculation above shows that the annual accumulation rate of ^{210}Pb is very much less than the range expected from measured annual atmospheric fluxes. The input of ^{210}Pb to the sediments has therefore not been constant which could reflect inconsistent delivery or inefficient trapping of ^{210}Pb.

The low levels of ^{210}Pb at this site are therefore probably associated with some degree of sediment resuspension and deposition. They may also be associated with the catchment disturbance which occurred during the 1960s and 70s, and overall lack of trap efficiency. This is returned to in the summary (section 5.4) where all of the analyses are discussed.

5.2.7 Particle size

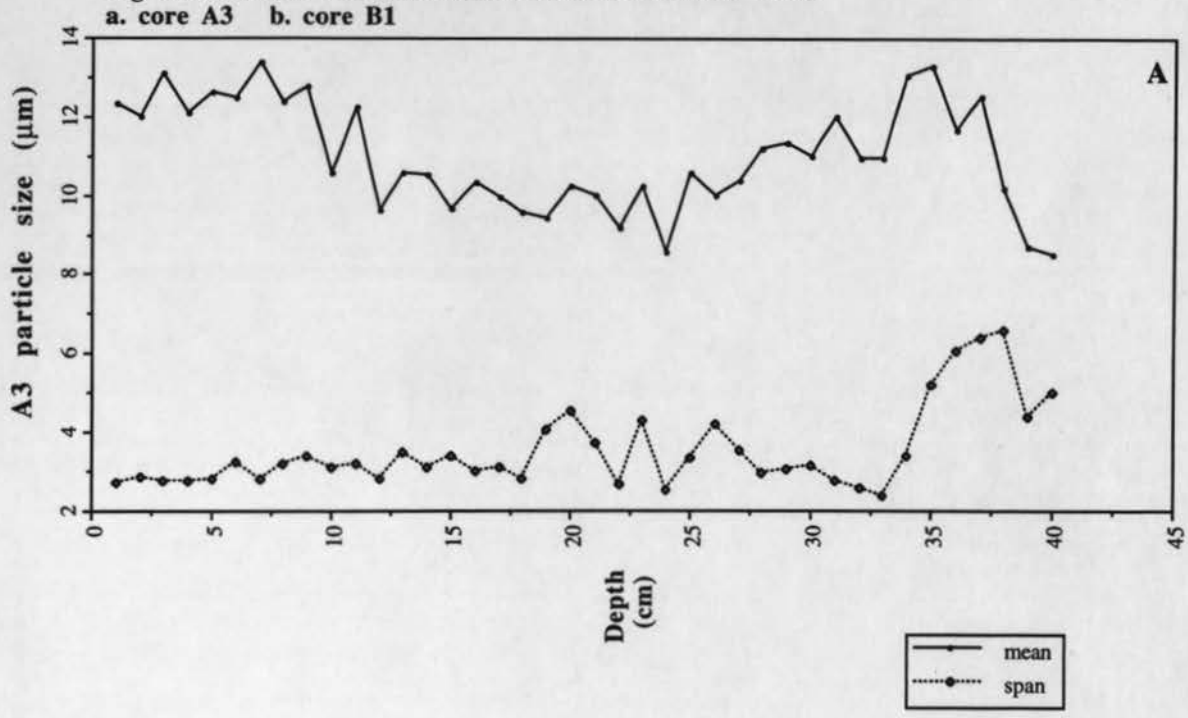
Particle size analysis was carried out on two cores from Wyken Pool, cores B1 and A3. It was not possible to carry out particle size analysis on a core for which heavy metal data were available since there was insufficient sediment left after total digestion had been carried out.

Downcore variation in mean particle size and span, a measure of the spread of particles about the average, for cores A3 and B1 is presented in Fig 5.16 a and b. Core A3 is located on the northernmost transect, near the western inlet (Fig 2.7b). Core B1 is located at the eastern end of the B transect, near the eastern marsh and downstream of the eastern inlet (Fig 2.7b).

Mean particle size varies between 8 and 12 μm in core A3, and the trend is for slightly decreasing particle size with depth. Between about 11 and 27 cm mean particle size becomes constant at an average of 10 μm before increasing again into the basal lake sediments. Span varies slightly in the top 19 cm of the lake core, but down to 28 cm varies between 5 and 9 μm. As the former soil is sampled, span increases to over 12.

The top 40 cm of core B1 shows slightly greater variability than core A3, as particle sizes vary between 7 and 13 μm. Particle size increases with depth in core B1 until about 20 cm where mean particle size decreases (average 8 μm). At about 40 cm depth in core B1, particle size begins to increase, reaching 30 μm at a depth of 60 cm. The buried soil

Fig 5.16 Particle size distribution in lake sediment cores
a. core A3 b. core B1



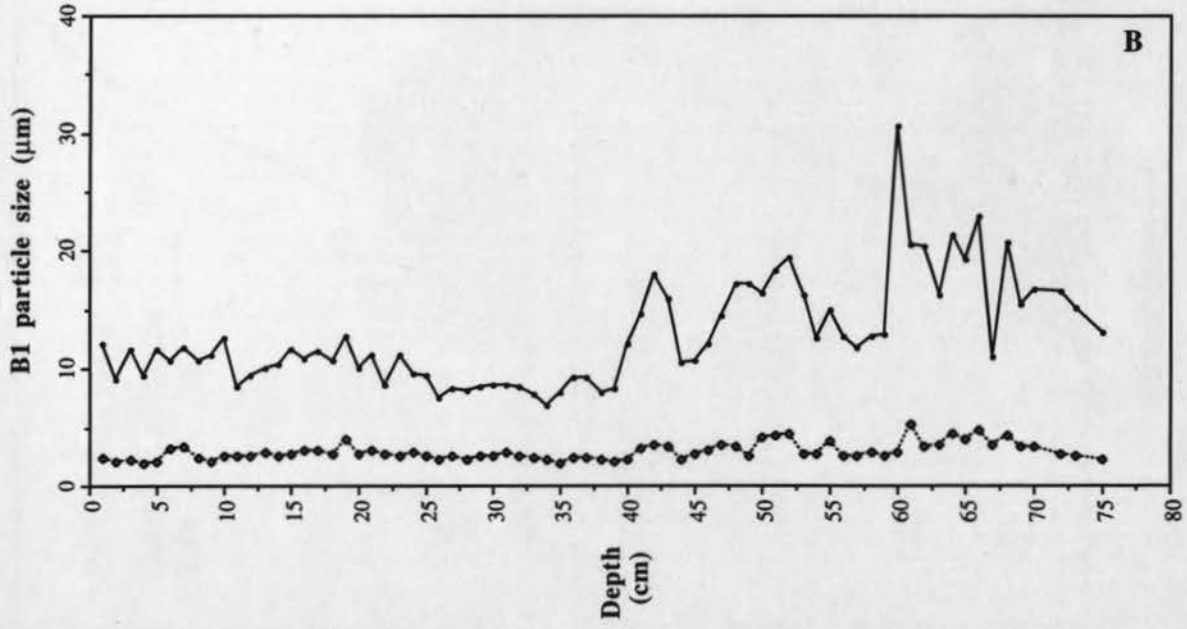
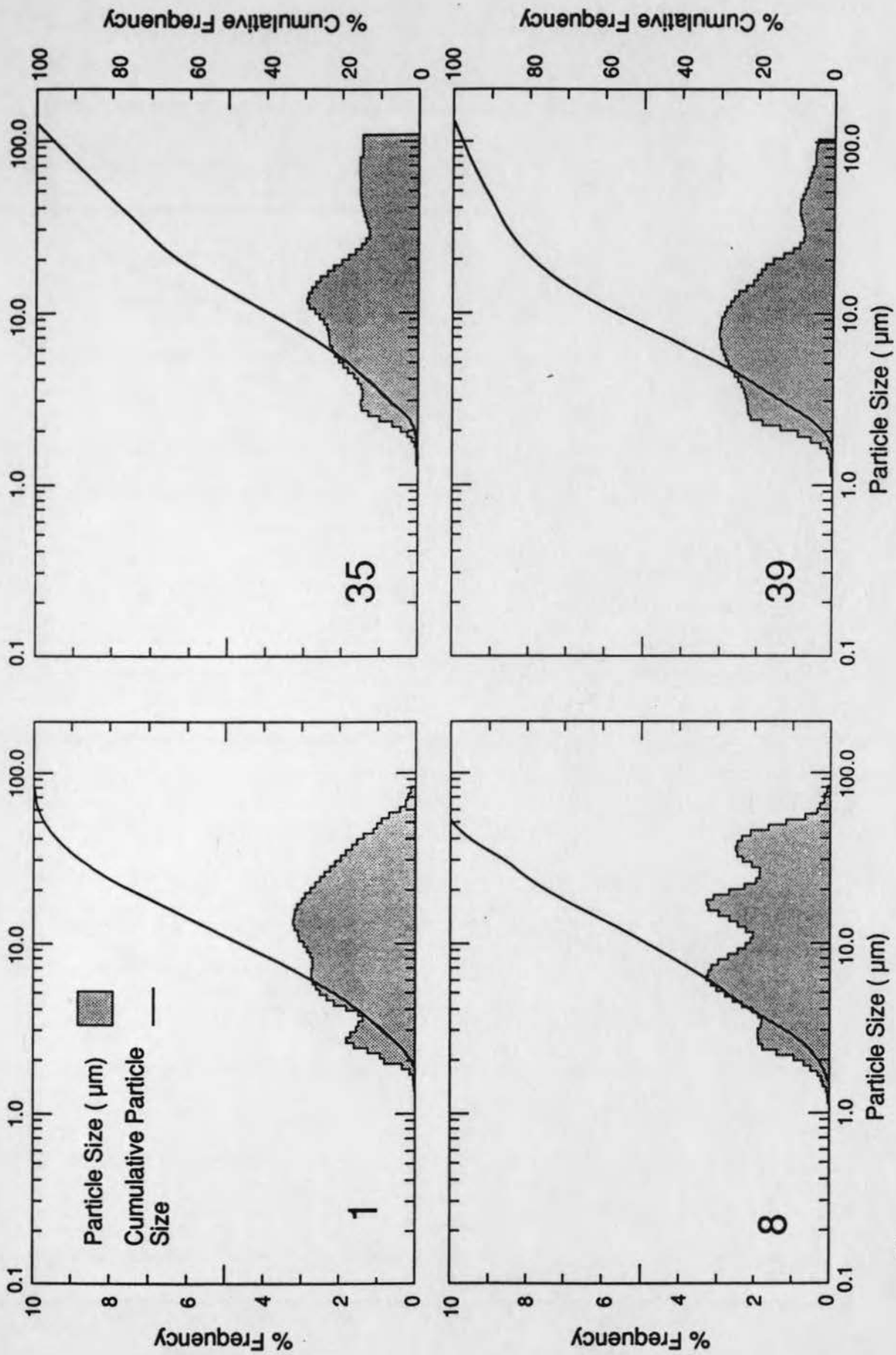
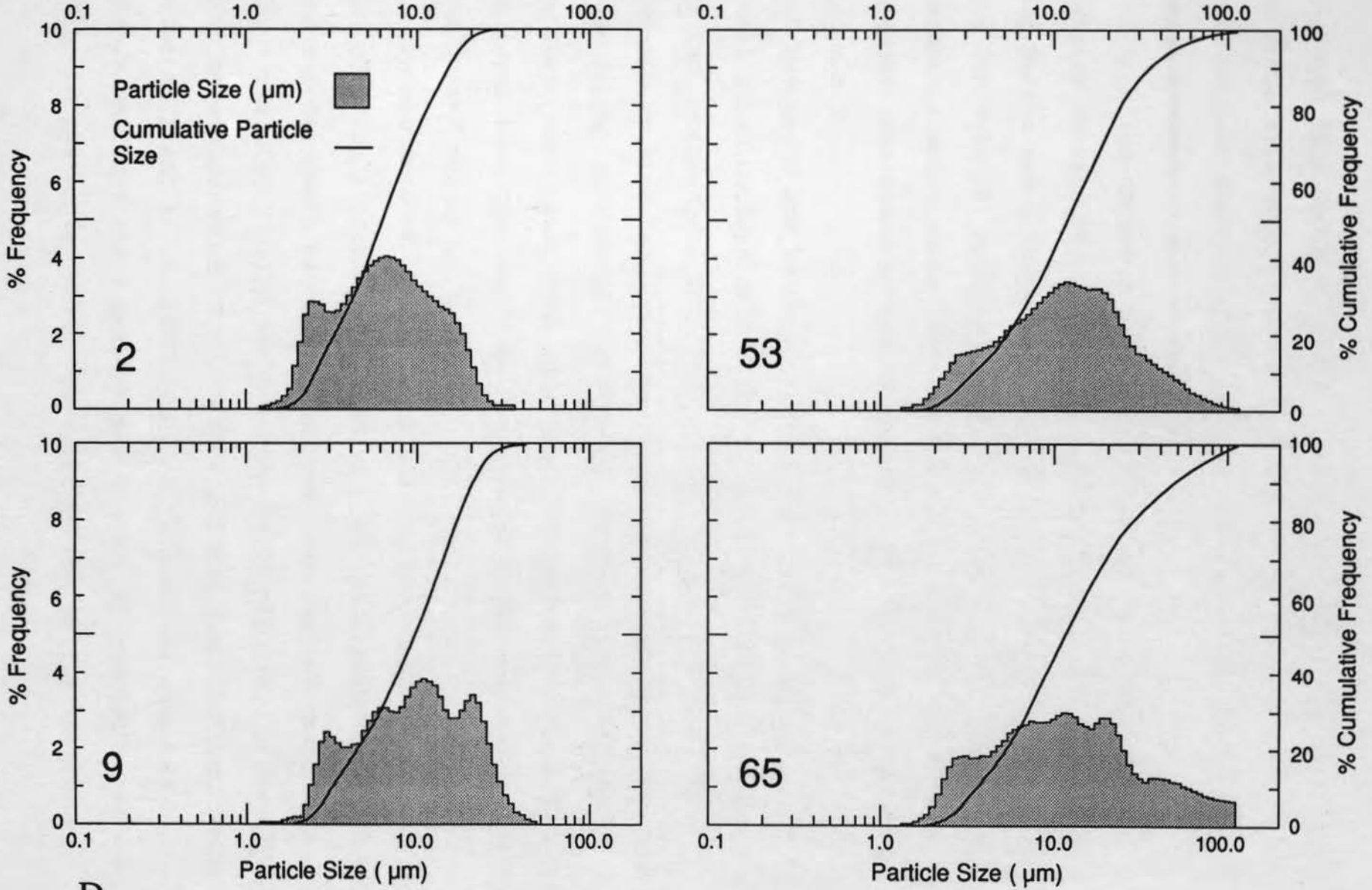


Fig 5.16 Examples of the multimodal character of individual lake sediment samples

c. core A3

d. core B1




Particle Size (μm)
Cumulative Particle Size
% Frequency
% Cumulative Frequency
Particle Size (μm)
0.1
1.0
10.0
100.0
2
53
9
65

D

is found at a depth of 65 cm in core B1, within which the mean particle size generally declines. The trend for span reflects that of mean particle size, again with a decrease in value between about 20 and 40 cm depth.

Examples of Laser Granulometer traces from individual samples showing the distribution of particle size are shown in Fig 5.16 c and d for cores A3 and B1 repectively. Both cores are dominated by multimodal particle size distributions with between 1 and 4 peaks. The top 5 samples of both cores are bimodal, dominated by the 15 μm (core A3) and the 10 μm peaks (core B1).

Between 5 and 35 cm in core A3 the profile has 3 or 4 modal distributions with peaks in particle size at 3, 7 and 15 μm and, where there is a fourth peak, 40 μm. The tail above the 100 μm size indicates the percentage of grains in the fine sand range; 100% of all grains sampled from within the lake sediment were finer than fine sand. The samples from 35 to 39 cm depth show the 'tail' as coarser particles are samples in the former soil.

In the case of core B1 (Fig 5.16 c) the samples are mainly dominated by a bimodal distribution, but also with some 1, 3 and 4 modal peaks without any discernable pattern downcore. Where the distribution has a single mode, the peak in particle size occurs at about 10 μm. With a bimodal distribution, peaks occur at 3 and 10 μm. Additional peaks occur at sizes of 20 and 40 μm for 3 and 4 peaks respectively. At the bottom of the core, in the buried soil, the distribution shifts to coarser

particle sizes. Fig 5.16 c illustrates the 'tail' in particle size which occurs as the former soil is sampled at 65 cm depth and also shows the particle size distribution of three samples taken from the lake sediment.

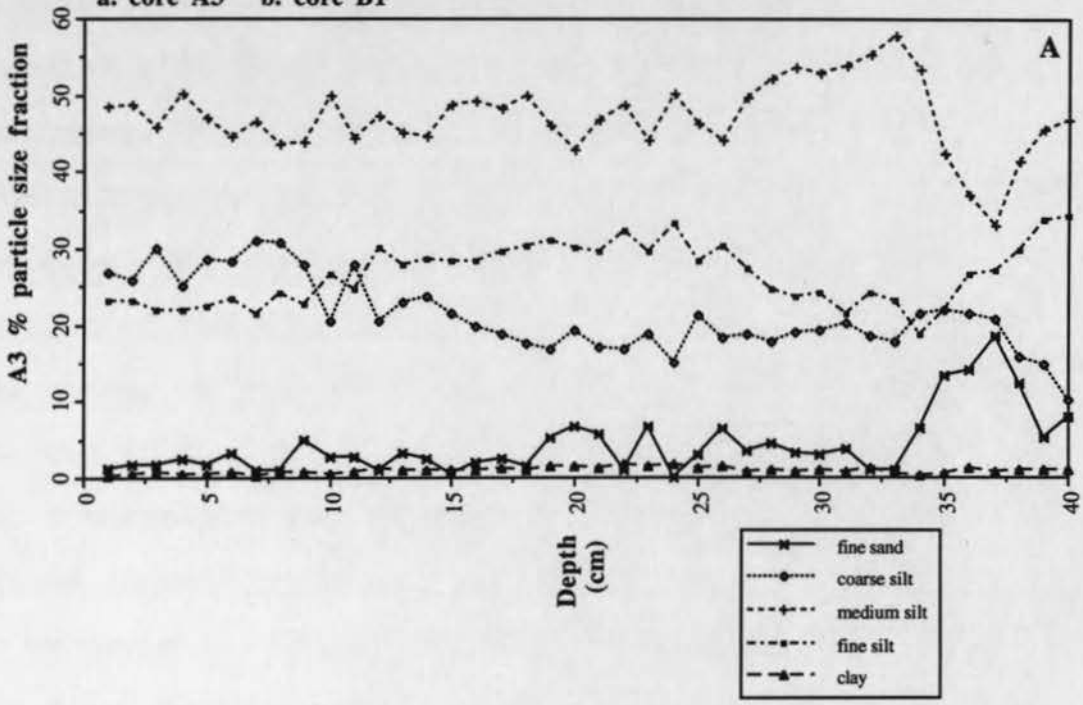
There is very little fine sand or clay (above 63 μm and below 2 μm respectively) in either core (Figs 5.17 a and b). Just above the soil in core B1 the percentages of both increase slightly, whereas in core A3, the proportion of fine sand increases from just above zero to 20% at 37 cm, just above the soil/sediment interface.

The trends of medium and coarse silt are similar in core B3, although the increase at 32 cm in the medium silt fraction is not matched by that in the coarse silt of core A1.

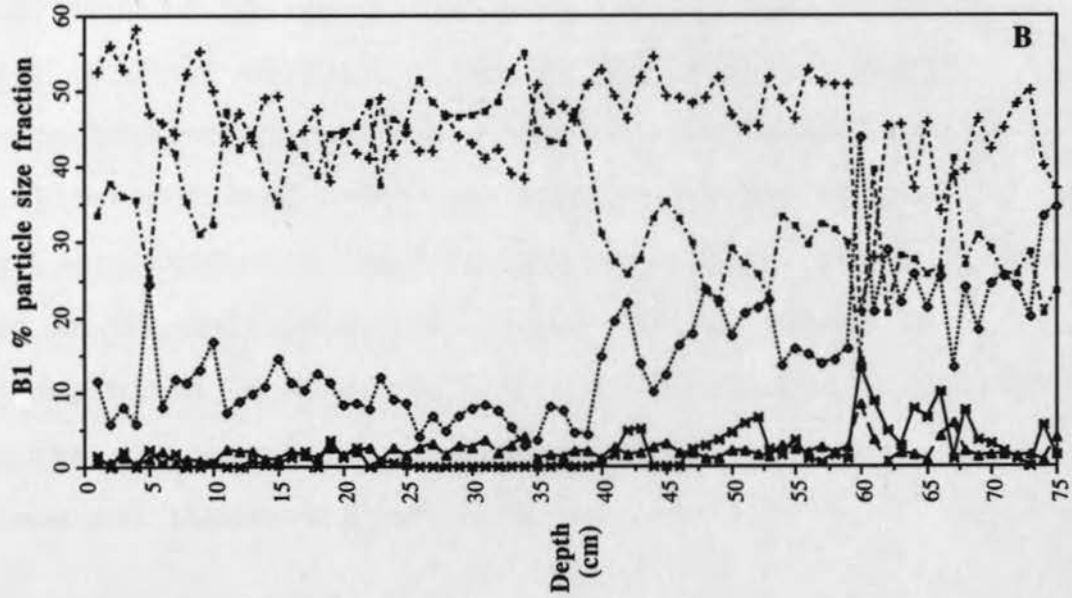
The proportions of fine and medium silt in core B1 increase down to 38 cm. That of medium silt continues to increase to 60 cm when it declines slightly before increasing again in the basal soil. At 38 cm the proportion of fine silt declines to a level which is maintained to 60 cm depth after which the percentage fluctuates markedly within the basal soil. The plot for coarse silt parallels that of the fine silt; declining in the upper 38 cm and rising in proportion down to a depth of 60 cm.

In core A3, the proportions of fine and coarse silt also parallel one another. The latter increases slightly down to a depth of 24 cm and the former exhibits a small increase. The trends are reversed in the subsequent 10 cm, with the lower 6

Fig 5.17 Percentage change in particle size with depth
a. core A3 b. core B1



Depth of former soil surface
A3 = 40 cm, B1 = 30 cm



cm showing a marked decline in the percentage of coarse silt with a corresponding increase in the fine silt content.

In both cores, the dominant fraction in the lake sediment is the medium silt which comprises approximately 50% of the total sediment. This is closely followed by the fine silt which contributes up to 25% in core A3 and 35% in core B1. The clay and fine sand contribute least to the particle size distribution of the sediment.

The change in mean particle size in core A3 (Fig 5.16 a) is reflected in a slight decrease in the proportion of fine silt and a corresponding increase in the coarse silt fraction. The changes in mean particle size in core B1 shown in Fig 5.16 b at 20 cm depth are not reflected in the percentage change in particle size. However, at 40 cm there is an increase in the proportion of coarse silt at the expense of the fine silt fraction.

Particle size analysis appears to show a change in sedimentation in both cores between 11 and 27 cm depth (core A3) and between 20 and 40 cm depth (core B1). This confirms evidence from other analyses, such as bulk density, heavy metal concentration and mineral magnetic characteristics, that Wyken Pool has suffered catchment disturbance in the past, probably associated with construction activities, which is now reflected in the sediments. The subject of the change in sediment deposited in Wyken Pool will be considered in Chapter 6.5 when the characteristics of the catchment components will be reviewed and likely sources assessed.

5.3 Statistical analysis

Statistical analysis was carried out on a number of data sets from Wyken Pool:

The 16 lake cores separately
The 16 surface samples
The 16 lake cores together
The 4 lake cores with heavy metals data together
The 4 lake cores with heavy metals data separately.

Chapter 2, Fig 2.21 shows the range of analysis carried out on these data sets. Descriptive statistics, skewness, kurtosis and correlation were calculated on all the above. Regression was carried out on selected data sets as explained in section 5.3 a below. Principal Component Analysis (PCA) was carried out on the 4 lake cores with heavy metals data separately. The conventions followed for statistical testing of the data from Wyken Pool are the same as for Swanswell Pool (Chapter 4.3). All statistical tests were carried out on the raw data sets since the data set approximated a normal distribution (Chapter 4.3).

The results of statistical analysis is divided into two subsections, firstly, covering descriptive statistics, correlation and regression and secondly a description of the results obtained from PCA.

a. Descriptive statistics, correlation and regression

This is divided into three parts in order to determine the relationships between mineral magnetic parameters and those between heavy metals, whether there is any relationship between heavy metals and mineral magnetic characteristics of the sediment and whether mineral magnetism can be used as a predictive tool in urban lakes.

Table 5.10 summarises the mean, minimum and maximum of analyses from Wyken Pool.

i. The relationship between mineral magnetic parameters in lake sediment cores and surface samples.

Correlation matrices between magnetic parameters highlight a high level of interdependance in a similar way to that found in the data from Swanswell Pool. Table 5.11 a illustrates this with a correlation matrix taken from the sum of all the cores analysed in Wyken Pool.

With a critical R value for the correlation coefficient of 0.0815, correlations between measured parameters such as χ_{lf} and SIRM are consistently high. Correlations between derived parameters such as HIRM, χ_{fd} and S-ratio are also highly significant.

Table 5.10 Summary descriptive statistics of the lake sediments from Wyken Pool (n=233)

Variable	Mean	Minimum	Maximum
χ_{lf} [1]	0.19	0.0	0.6
χ_{fd} [2]	9.15	0.0	171.8
SIRM	3.57	0.3	22.3
S ratio	0.71	0.1	1.0
HIRM[3]	0.48	0.0	7.7
DBD[4]	0.49	0.1	1.1
WBD[4]	1.34	0.9	1.7
DWR	0.36	0.1	0.8
Fe[5]	17.13	6.3	32.2
Mn[5]	0.58	0.1	1.2
Fe/Mn	32.97	15.2	80.0
Cd[6]	6.84	0.0	29.7
Pb[6]	126.65	0.0	761.3
Ni[6]	60.31	0.0	201.6
Zn[6]	451.78	2.2	2071.3
Cu[6]	26.26	2.0	281.1
P[6]	251.88	0.0	998.7
Na*[5]	1.67	1.3	2.1
K*[5]	17.09	9.0	29.3
Ca*[5]	40.4	0.5	110.4
Mg*[5]	7.92	0.5	13.5

* n=31

Units
[1] $\mu m^3\ kg^{-1}$
[2] $nm^3\ kg^{-1}$
[3] $mAm^2\ kg^{-1}$
[4] $g\ cm^{-3}$
[5] $mg\ g^{-1}$
[6] $\mu g\ g^{-1}$

DBD = dry bulk density
WBD = wet bulk density
DWR = dry / wet ratio

Table 5.11 a Wyken Pool correlations between mineral magnetic parameters from all lake cores. (n = 284, r = 0.0815 at 99%).

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
χ_{lf}	-						
χ_{hf}	0.9992**	-					
χ_{fd}	0.3232**	0.3181**	-				
SIRM	0.7899**	0.7953**		-			
IRM	0.7814**	0.7837**	0.1709*	0.9285**	-		
HIRM	0.4882**	0.5006**		0.7162**	0.5438**	-	
S-ratio	0.1506*	0.1492*			0.1712*	0.2498**	-

ii. Relationship between heavy metals in lake sediment cores and surface sediments.

There is a high level of correlation between the individual heavy metals. Table 5.11 b presents the correlation matrix between heavy metals from the individual lake sediment cores for which there is heavy metal data in Wyken Pool. In all of the cores, except BO, all the heavy metals correlate

Table 5.11b Wyken Pool correlation between heavy metals in lake cores

a.) Core AO (n=60, critical R=0.25 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.8125**	-			
Zn	0.9005**	0.8533**	-		
Pb	0.8549**	0.8853**	0.9362**	-	
Cu	0.8611**	0.8185**	0.985**	0.931**	-

b.) Core BO (n=65, critical R=0.241 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.3911**	-			
Zn	0.9515**	0.2966*	-		
Pb	0.8542**	0.3239*	0.8561**	-	
Cu	0.3185*	0.6212**	0.2881*		-

c.) Core CO (n=61, critical R=0.25 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.4657**	-			
Zn	0.8745**	0.7066**	-		
Pb	0.6907**	0.5556**	0.8314**	-	
Cu	0.6836**	0.5723**	0.825**	0.9766**	-

d.) Core DO (n=51, critical R=0.2732 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.7446**	-			
Zn	0.7738**	0.7081**	-		
Pb	0.6177**	0.4402**	0.773**	-	
Cu	0.8651**	0.7081**	0.8619**	0.8739**	-

Table 5.11 b (continued) Wyken Pool correlation between heavy metals

e.) Combined lake cores (n=284, critical R = 0.0815 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd					
Ni	0.6274**	-			
Zn	0.8847**	0.6988**	-		
Pb	0.7409**	0.6403**	0.8621**	-	
Cu	0.6462**	0.5895**	0.7907**	0.8195**	-

** denotes significance of 99.9%
* denotes significance of 99%

f.) Surface lake samples (n=16, critical R=0.4973 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni		-			
Zn					
Pb			0.6508*	-	
Cu		0.7267*			

Table 5.11 c Wyken Pool correlations between heavy metals and mineral magnetic parameters in lake cores.

a.) Core AO (n=60, critical R=0.2108 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.7395**	0.7397**	0.8776**	0.3367**	0.4797**		
Ni	0.6391**	0.6396**	0.6332**				
Zn	0.7317**	0.7319**	0.7781**	0.3325*	0.4536**		
Pb	0.6516**	0.6503**	0.7562**		0.3396*		
Cu	0.6642**	0.6646**	0.744**		0.4160**		

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b.) Core BO (n=65, critical R=0.241 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.2945*	0.2945*					
Zn	0.4000**	0.4000**	0.3345*				
Pb	0.2993*						

No correlation with Cu or Ni

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c.) Core CO (n=61, critical R=0.25 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.4334**	0.4334**		0.4639**	0.4514**	0.3764**	
Ni	0.4218**	0.4218**		0.4498**	0.3613*	0.5096**	
Zn	0.5055**	0.5055**		0.5311**	0.5132**		
Pb	0.3596*	0.3596*		0.3779*	0.3778*		
Cu	0.4331**	0.4331**		0.4490**	0.4445**	0.3382*	

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d.) Core DO (n=51, critical R=0.2732 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Ni	0.4121*	0.4121*					

No correlation with Cd, Zn, Pb or Cu

---

with one another at the 99.9% significance level. In the case of core BO, some of the heavy metals are only significantly correlated at the 99% significance level. Zn and Cd correlate highly in each of the cores and Cu and Pb correlate highly in all cores except BO. When all the lake cores are taken together (Table 5.11 b), all the heavy metals correlate with each other at the 99.9% significance level. Zn and Cd have the highest correlation coefficient of 0.8847.

Also on Table 5.11 b are the correlation coefficients of the top 1 cm samples from Wyken Pool. These show little correlation between the heavy metals with the exception of Pb with Cd and Zn, and Ni with Cu, but these three are only significant at the 99% level.

Correlations between the heavy metals are thus inconsistent, especially in the surface samples, although the relationship between Cd and Zn cited in the literature (Monahan, 1993) and discussed in Chapter 2.5ii does seem to be present in sediment cores in Wyken Pool, but not in the surface samples.

Comparison with data from Swanswell Pool shows that the results from each site are different and therefore site-specific. This is exemplified by the lack of a relationship between Cd and Zn in the lake sediment cores from Swanswell Pool, but the presence of such a relationship between the two elements in the cores from Wyken Pool. This would seem to preclude the general use of one heavy metal in predicting the presence of another heavy metal in lake sediments.

iii. Correlation and regression between heavy metal concentration and mineral magnetic parameters

Table 5.11 c gives the correlation matrices of heavy metals with magnetic parameters for individual lake cores. There is little correlation shown in either cores BO or DO. In the case of BO, correlation with χ_{lf}, χ_{hf} and χ_{fd}, is shown with Cd, Zn and Pb, but only that between Zn and χ_{lf} are significant at the 99.9% level. In the case of core DO, the only significant correlation is between χ_{lf}, χ_{hf} and Ni. Core AO shows the highest and most significant correlation between heavy metals, χ_{lf}, χ_{hf} and χ_{fd}, with low correlation between metals, SIRM and IRM. Core CO shows little correlation between metals and the derived magnetic parameters, such as HIRM and the S-ratio, with lower and less significant correlations between χ_{lf}, SIRM and related measured parameters than that shown in core AO.

The top 1cm of the grid of lake cores shows little correlation between heavy metals and magnetic parameters, with Pb and the S-ratio correlating at the 99% level and no correlation between the other heavy metals.

In the bulk data set, all metals, with the exception of Ni, correlate at the 99.9% level with the χ_{lf} related magnetic parameters, and Ni correlates at the 99% level with SIRM, IRM and HIRM.

Regression was carried out between heavy metals and magnetic parameters on individual cores. This was to determine whether mineral magnetic characteristics could be used to predict the levels of heavy metals in a sample. Cores AO and

Table 5.11 c (continued) Wyken Pool correlation between heavy metals and mineral magnetic parameters

e.) Combined lake cores (n=284, critical R=0.0815 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.2584**	0.2530**	0.2514**				
Ni				0.1824*	0.1404*	0.1974**	
Zn	0.3216**	0.3186**	0.2515**			0.1404*	
Pb	0.2445**	0.2416**	0.1534*				
Cu	0.2251**	0.2191**					

f.) Surficial lake samples (n=16, critical R=0.4973 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Pb							0.7450*

No correlation with Cd, Ni, Zn or Cu

CO were chosen as there was little correlation shown in cores BO and DO. From the correlations, the coefficient value with a significance of 99.9% and the highest values were selected, such as Cu with χ_{lf} in core CO (0.4331** see Table 5.11 c). The scattergrams are presented in Figs 5.18 to 5.20 with the associated values of explained variance and the regression equations. Chapter 4.3 aiii explains the theory behind the use of regression as a predictive tool.

R^2 values for core CO vary between 12.9 and 25.6%, which is not particularly high. Those for core AO explain between

Table 5.12 Varimax rotated factor matrix
(n = 16, critical R = 0.4973 at 99%)
a. Cores AO and BO
b. Cores CO and DO

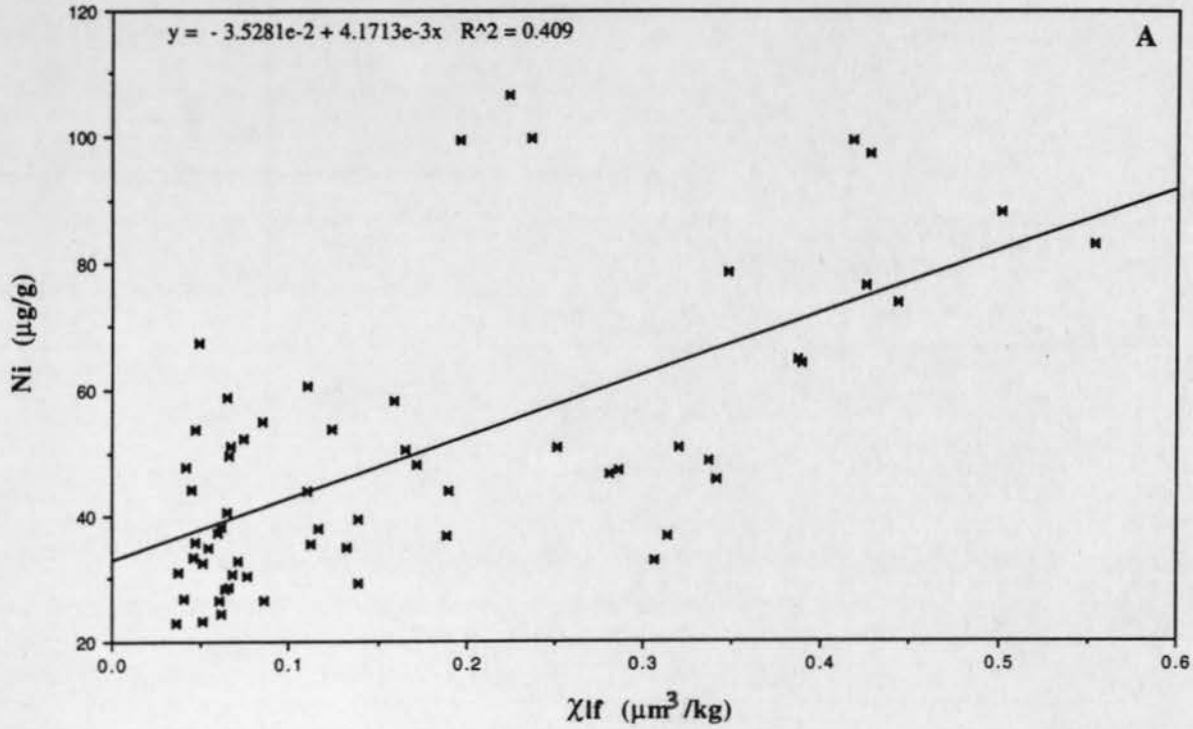
Rotated Factor Matrix:

	A	FACTOR 1	FACTOR 2	FACTOR 3
AO	LFX	.65779	.67745	.17997
	HFX	.65656	.68008	.17968
	FDX	.72063	.26107	.46731
	SIRM	.14970	.96847	.10016
	IRM	.28665	.68798	.51745
	HIRM	-.08247	.79449	-.42594
	S_RATIO	.11984	-.04522	.82416
	CD	.88438	.19189	.26550
	NI	.93761	.10144	-.11622
	PB	.94860	.07723	.07548
	CU	.90059	.11706	.19998
	ZN	.92899	.16788	.18418
	FE	.87291	.35808	-.09789
	MN	.97194	.14915	-.10692
	FE_MN	-.78746	.00347	.38944
	P	-.12879	.08200	.77719
BO	LFX	.81252	.37353	-.38754
	HFX	.81252	.37353	-.38754
	FDX	.15905	.41190	-.12735
	SIRM	.97814	-.08082	-.04694
	IRM	.98269	.06279	-.03751
	HIRM	.95803	-.15248	.04015
	S_RATIO	.44555	.25128	-.45164
	CD	.09295	.90451	.21204
	NI	-.21239	.43600	.67957
	PB	.02977	.88803	.03069
	CU	-.19068	.35421	.48549
	ZN	.09415	.94136	.01310
	FE	.44358	-.08349	.81616
	MN	-.18854	.84414	.19424
	FE_MN	.61710	-.49545	.45323
	P	.15963	-.04600	-.69613

Rotated Factor Matrix:

	B	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
CO	LFX	.95315	.25644	-.08203	.05065
	HFX	.95315	.25644	-.08203	.05065
	FDX	.57944	.08156	.45297	.31056
	SIRM	.93913	.28208	-.11470	-.00087
	IRM	.90175	.26859	-.13572	.20854
	HIRM	.83507	.21602	-.05445	-.44546
	S_RATIO	.15460	.12301	-.26042	.87492
	CD	.25058	.79582	-.12403	.05782
	NI	.27791	.64019	-.07144	-.44241
	PB	.10354	.93310	-.06500	.08308
	CU	.18715	.91755	-.02836	.08171
	ZN	.28071	.90422	-.17595	-.01542
	FE	-.10195	-.01204	.93729	-.18499
	MN	.27309	.85900	.07892	-.01918
	FE_MN	-.29630	-.51411	.70715	-.14697
	P	.45485	.44170	-.17086	.10368
DO	LFX	.19727	.89394	.09094	-.33230
	HFX	.19727	.89394	.09094	-.33230
	FDX	.13202	.81286	.01288	.08109
	SIRM	-.08485	.82298	-.50064	-.06273
	IRM	-.02819	.91652	.03763	-.06538
	HIRM	-.11623	.28628	-.92543	-.02810
	S_RATIO	.11442	.33738	.88756	-.09868
	CD	.88461	.05262	.01994	.30253
	NI	.74342	.22658	.20666	-.13658
	PB	.85954	-.03388	-.04404	.25511
	CU	.84761	.12444	-.05646	-.13386
	ZN	.96585	.16885	.07736	.09186
	FE	.80148	-.11216	.14381	.51066
	MN	.93941	.05803	.21297	.04826
	FE_MN	.03947	-.25174	-.10369	.87907
	P	.50136	-.10441	.05751	.72793

Fig 5.18 Core AO regression
a. Ni with χlf b. Pb with χlf



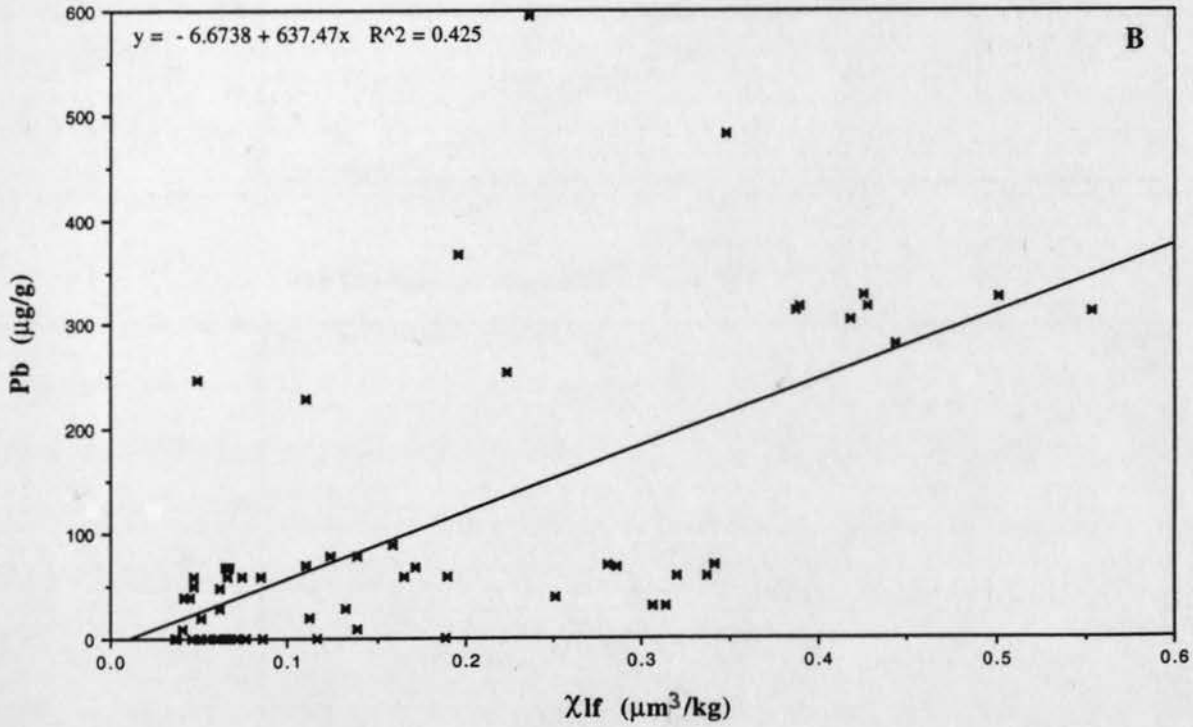
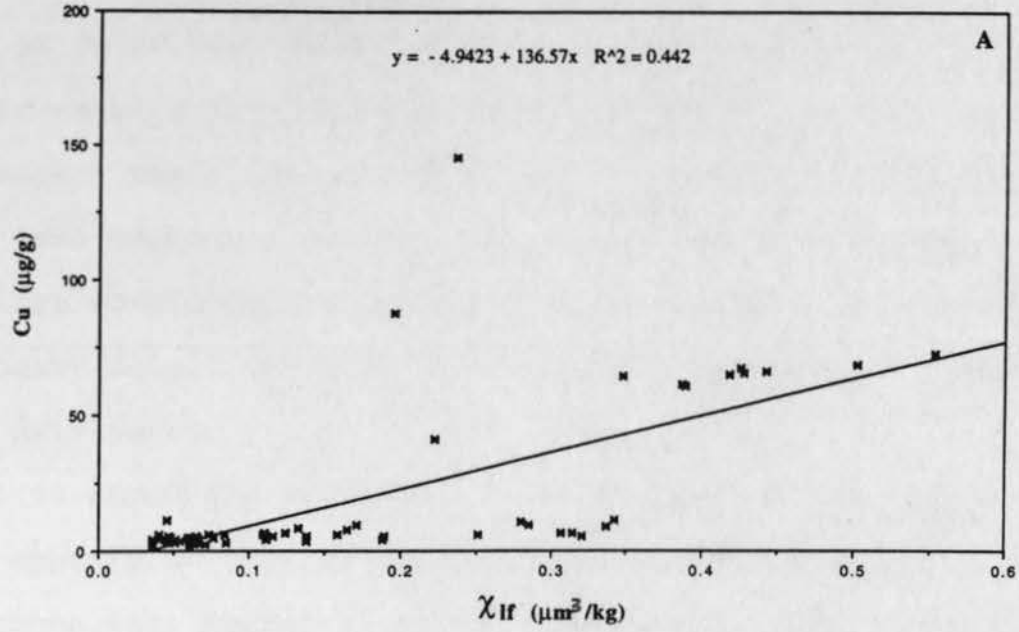


Fig 5.19 Core AO regression
a. Cu with χ_{lf} b. Zn with χ_{lf}



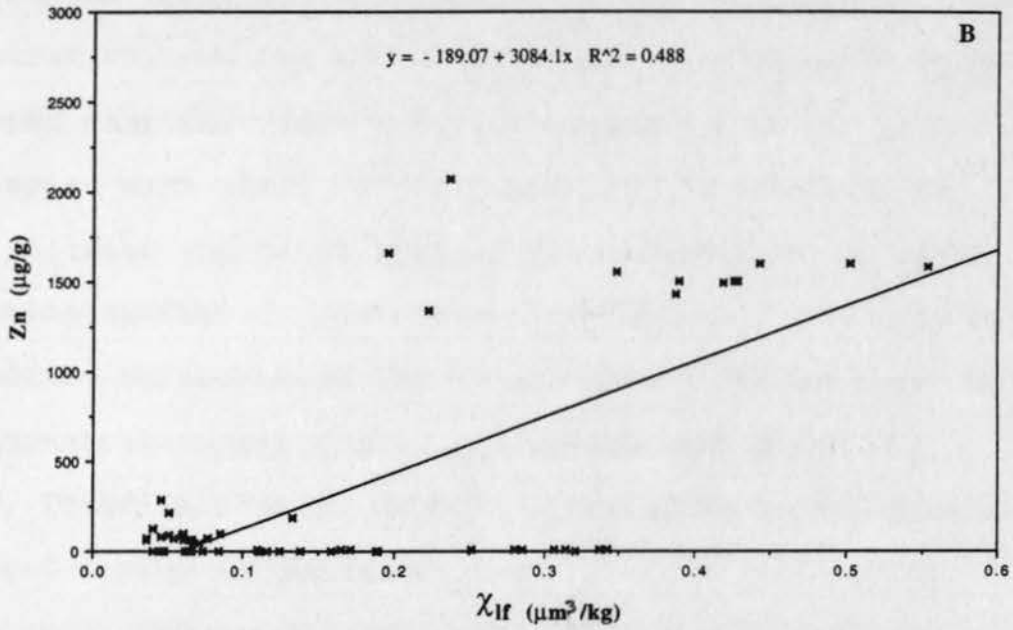
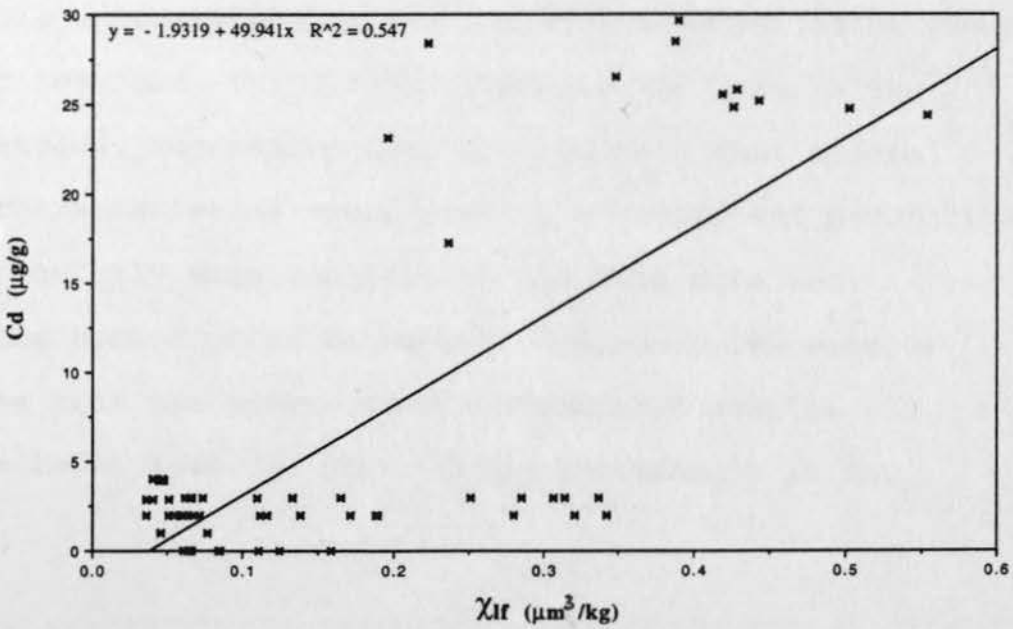


Fig 5.20 Core AO regression, Cd with χ_{lf}



40.9 and 54.7% of the variance and therefore there is a reasonable relationship between these parameters in this one core. However, the relationship is not consistent throughout the four lake cores and, if all the cores with heavy metals analysis are considered, there is no demonstrable relationship between heavy metals and mineral magnetic characteristics in the bulk data set.

Fig 5.20 shows the scattergram of χ_{lf} with Cd from core AO. This appears to resolve the samples into two distinct groups; those with higher Cd concentration and higher χ_{lf} values from the upper 13 cm of the core, and those with lower Cd concentration, some of whose χ_{lf} values overlap with those of the upper samples. There does not appear to be any pattern to the samples with lower Cd concentration. This effect is found to a lesser extent in some of the other plots of metal concentration against χ_{lf} as shown in Figs 5.18 b and 5.19 b, but the points representing the upper samples in the core, of higher concentration and higher χ_{lf} values, are more scattered. There is also no pattern discernable in the samples from greater depths in the core.

Correlation between heavy metals and magnetic parameters is therefore inconsistent at best, with a wide variation shown throughout the lake. This is particularly the case in the surface samples. Regression does not indicate that mineral magnetic characteristics would provide a consistent predictive tool, particularly when considering the bulk data set, although the scattergrams do appear to discern two sets of data; those from the upper, more contaminated samples and those from lower down the core. This relationship is not,

however, consistent for all the metals. Correlation of data from Swanswell Pool (Chapter 4.3) also indicated strong collinearity between mineral magnetic characteristics and between heavy metals. Regression of data from both sites does not provide evidence for the consistent use of mineral magnetic measurements as a surrogate for heavy metal analysis in these urban lake sediments.

b. Principal Component Analysis (PCA).

At Wyken Pool, as in the case of Swanswell Pool, PCA was applied to the lake sediment cores with heavy metals data and included all the other parameters measured such as bulk density and mineral magnetic characteristics.

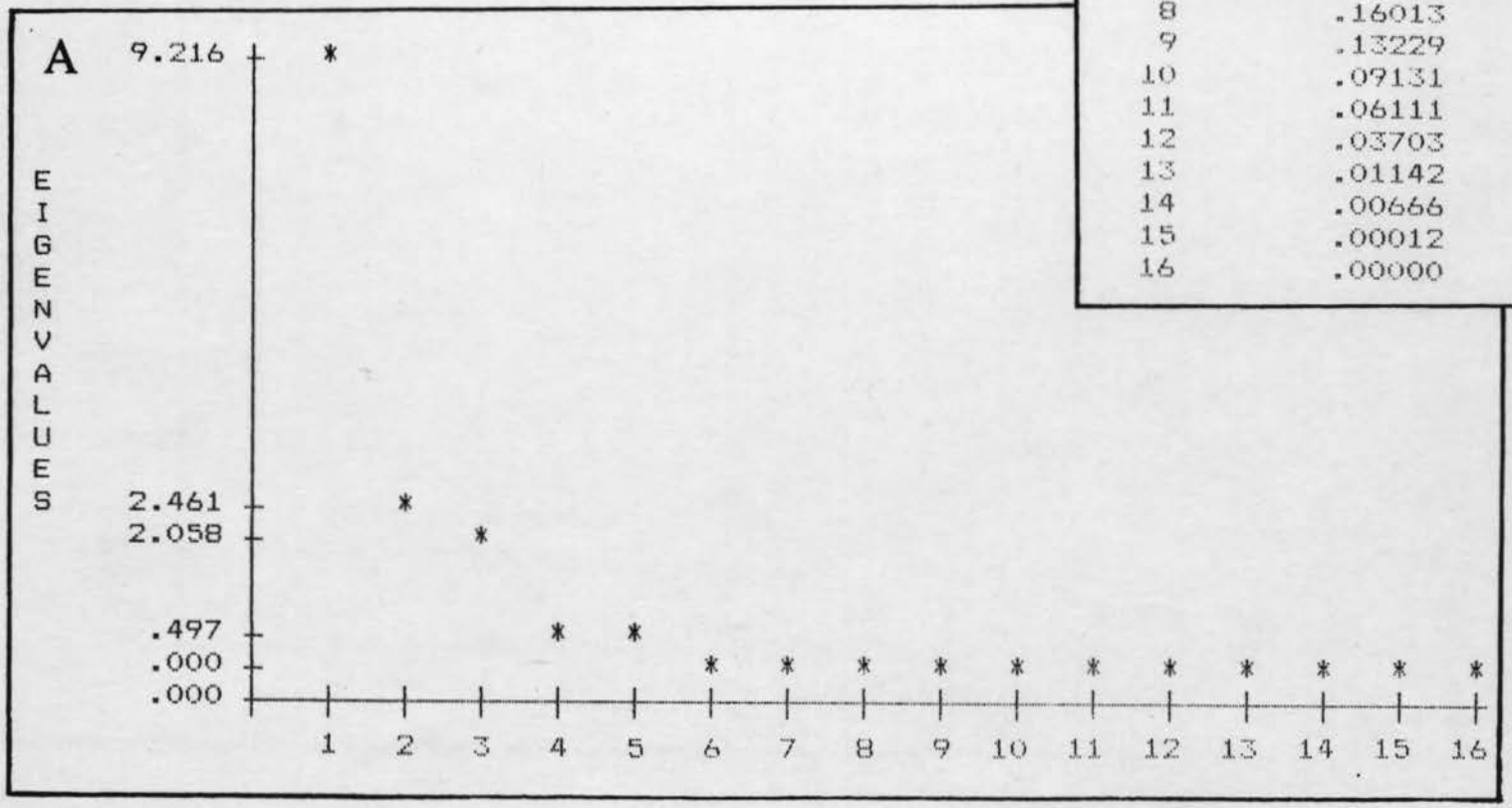
Tables 5.12 a and b present the varimax rotated factor matrices of the lake cores from Wyken Pool and Figs 5.21 a - d plot the eigenvalues obtained and the percentage contribution to the explained variance of the individual factors in the data set. In all the cores, the first two factors explained more than 60% of the variance (Table 5.13). The factor matrix plots utilised factors 1 and 2 only (Figs 5.22 a - d).

Table 5.14 summarises the parameters which dominate each factor. The distinction between magnetic characteristics and heavy metals in the 2 dominant factors serves to emphasise the lack of a relationship between these two properties in the lake sediments.

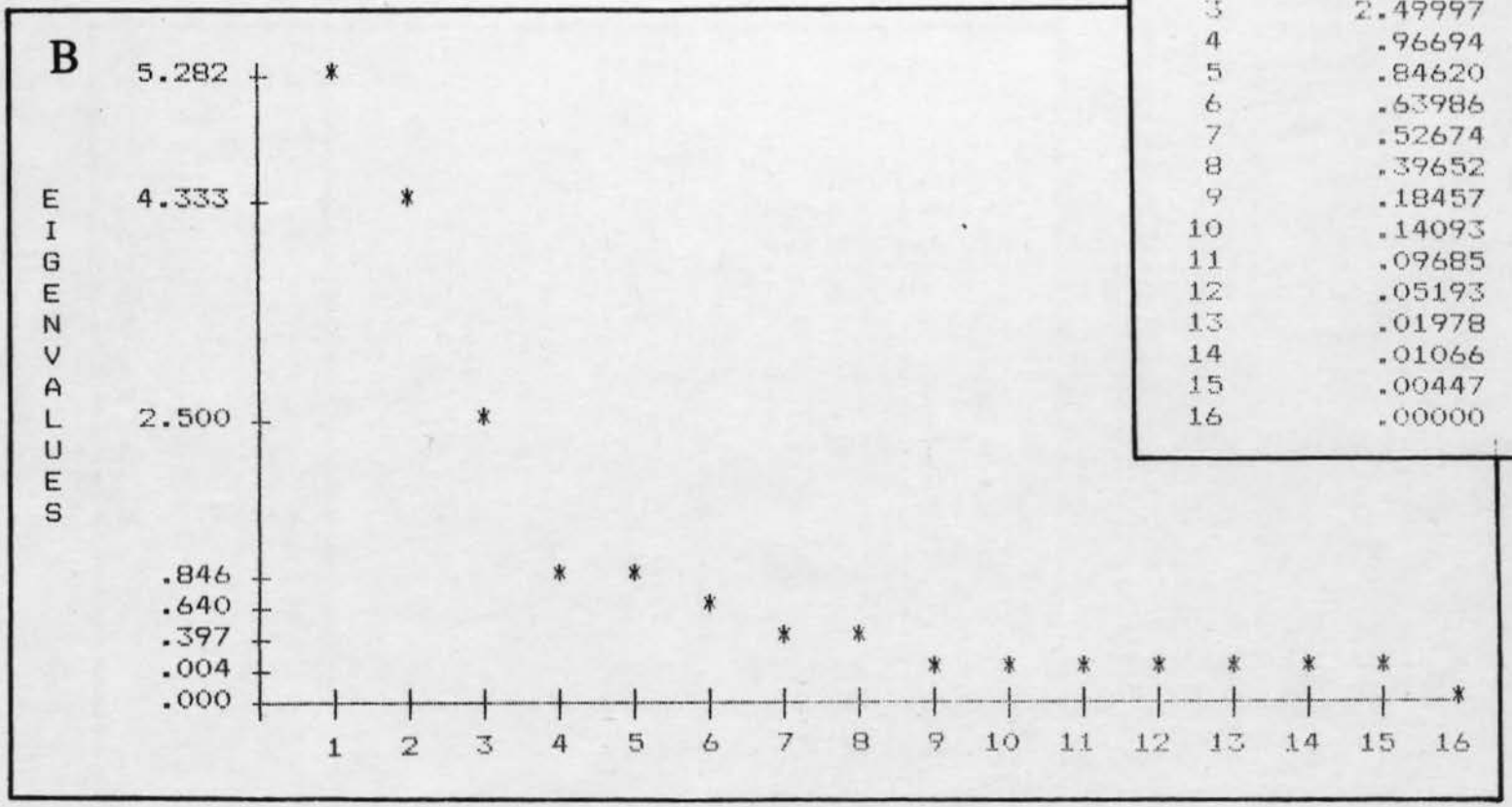
X-Y plots of the 2 dominant factors (Figs 5.22 a - d) indicate the strength of the relationship between these factors and the variables. Only the variables with the highest

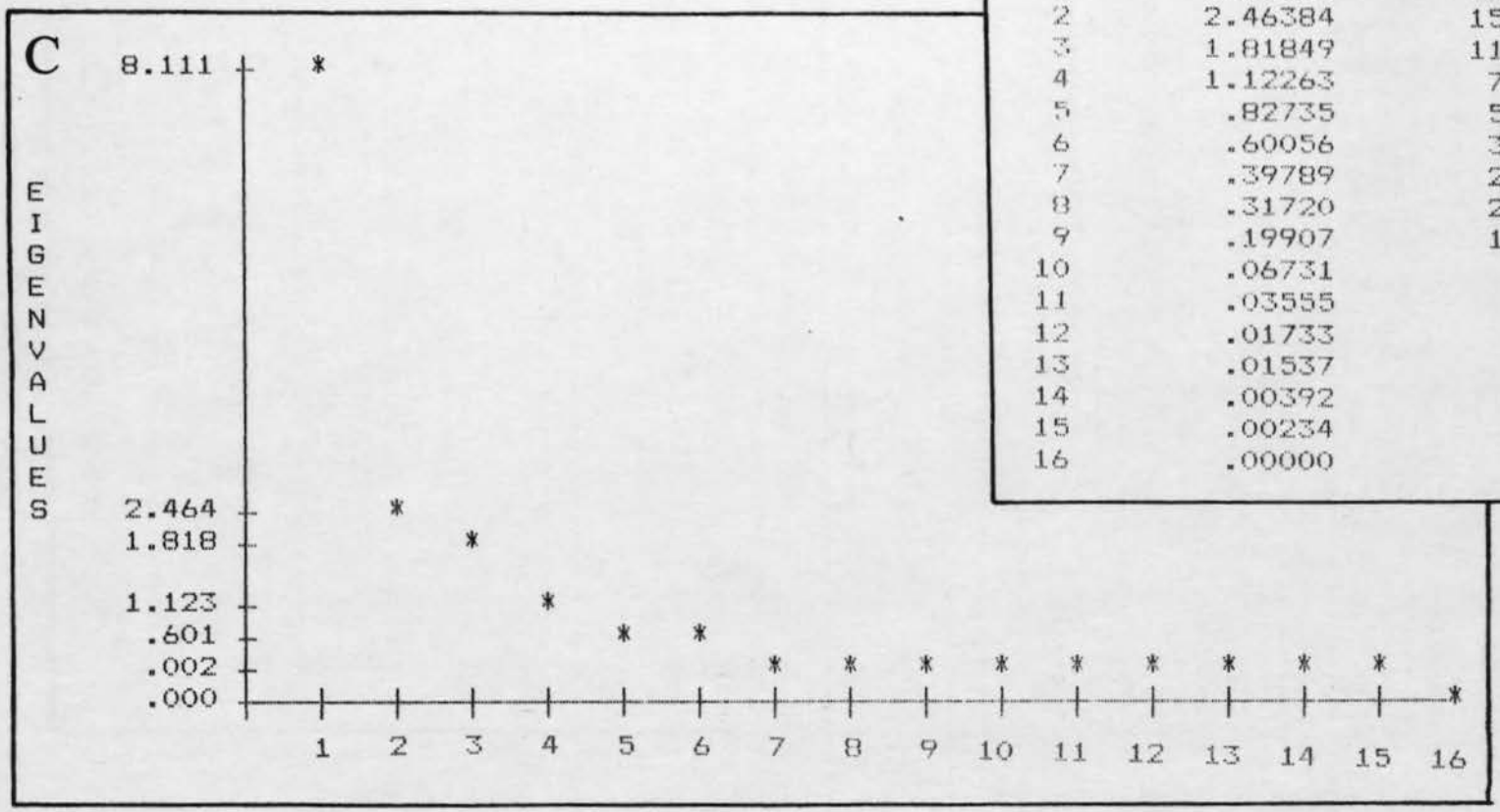
Fig 5.22 Eigenvalues
a. core A0
b. core B0
c. core C0
d. core D0

Factor	Eigenvalue	Pct of Var	Cum Pct
1	9.21616	57.6	57.6
2	2.46098	15.4	73.0
3	2.05826	12.9	85.8
4	.66328	4.1	90.0
5	.49684	3.1	93.1
6	.32716	2.0	95.1
7	.27726	1.7	96.9
8	.16013	1.0	97.9
9	.13229	.8	98.7
10	.09131	.6	99.3
11	.06111	.4	99.7
12	.03703	.2	99.9
13	.01142	.1	100.0
14	.00666	.0	100.0
15	.00012	.0	100.0
16	.00000	.0	100.0

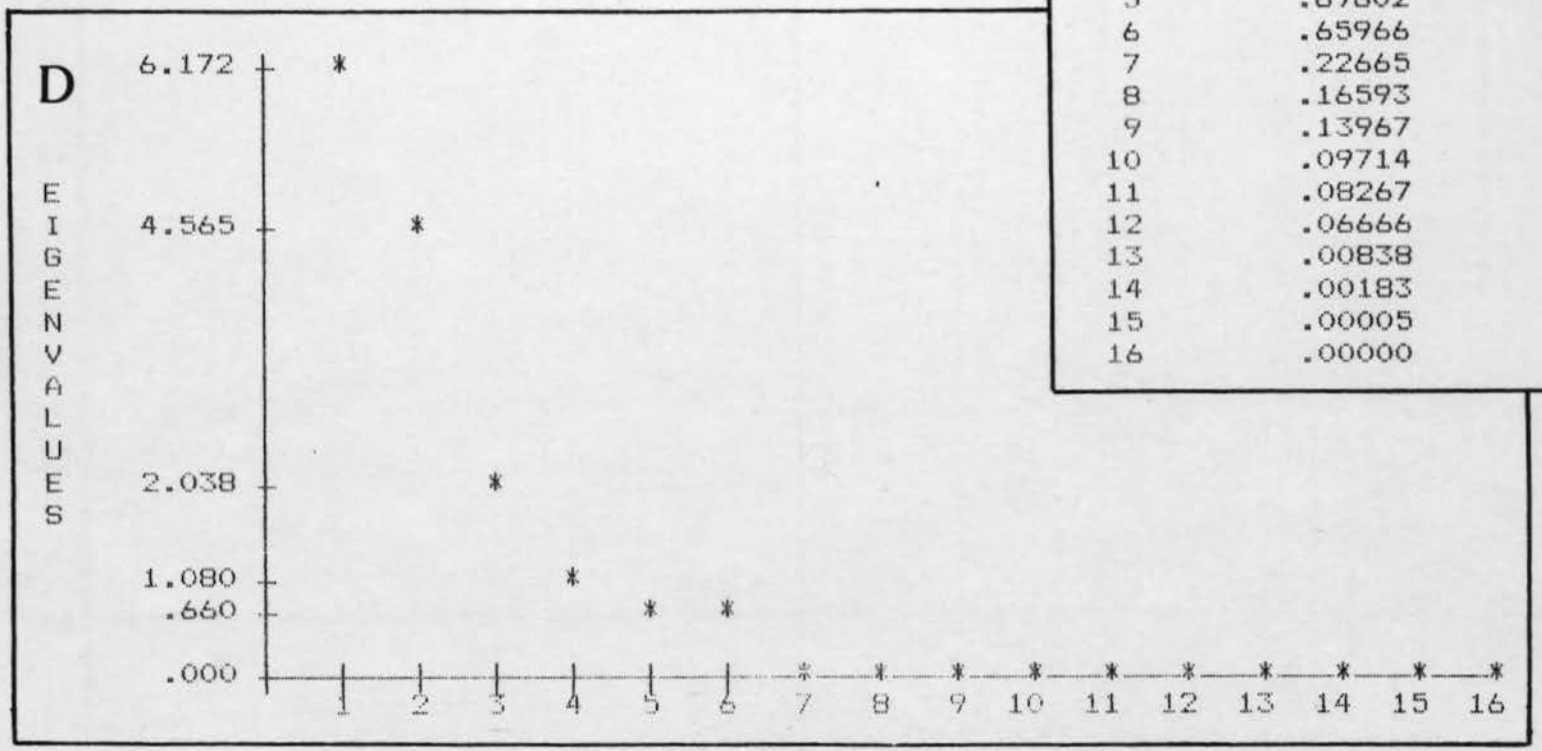


Factor	Eigenvalue	Pct of Var	Cum Pct
1	5.28191	33.0	33.0
2	4.33267	27.1	60.1
3	2.49997	15.6	75.7
4	.96694	6.0	81.8
5	.84620	5.3	87.0
6	.63986	4.0	91.0
7	.52674	3.3	94.3
8	.39652	2.5	96.8
9	.18457	1.2	98.0
10	.14093	.9	98.9
11	.09685	.6	99.5
12	.05193	.3	99.8
13	.01978	.1	99.9
14	.01066	.1	100.0
15	.00447	.0	100.0
16	.00000	.0	100.0



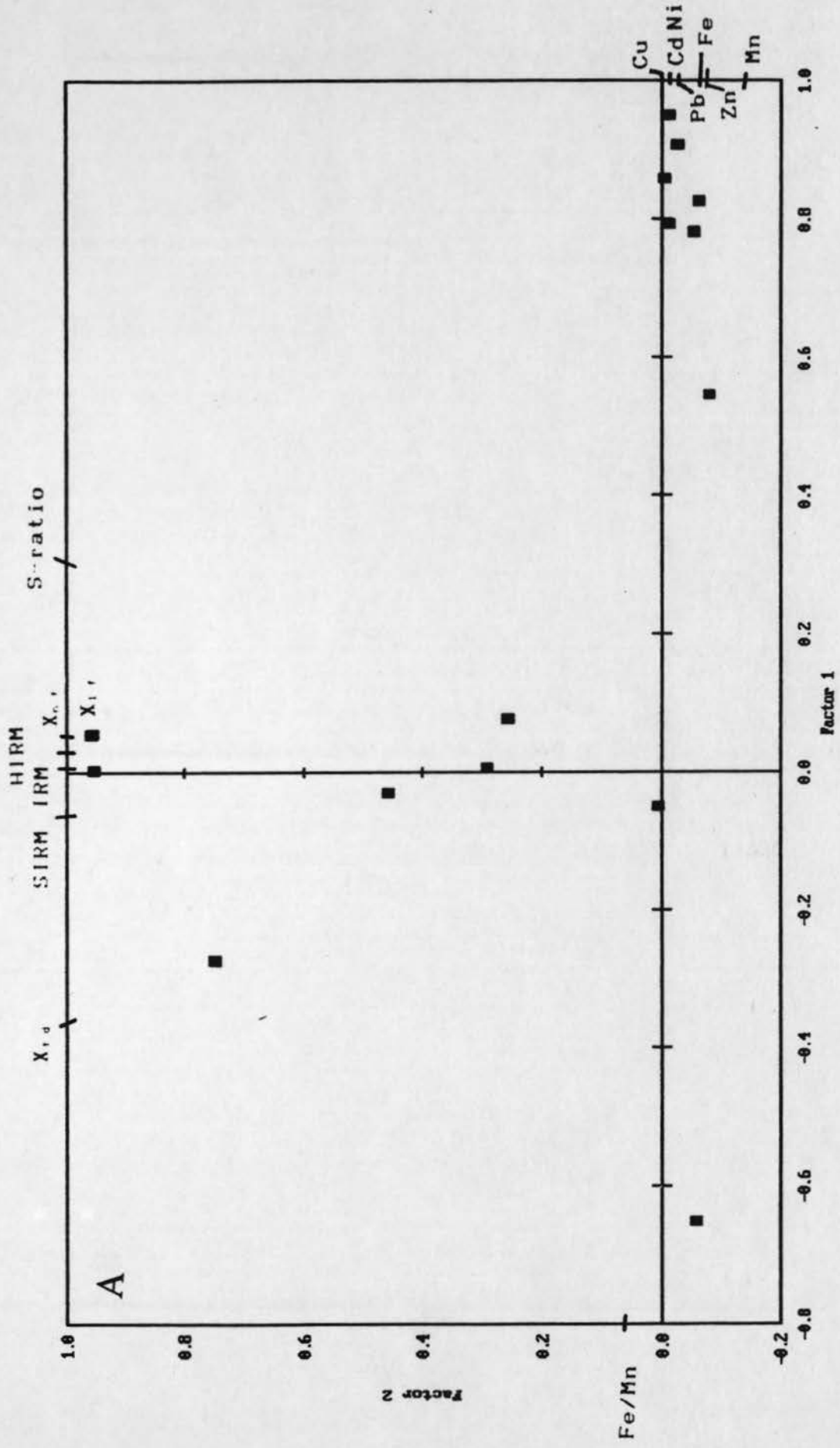


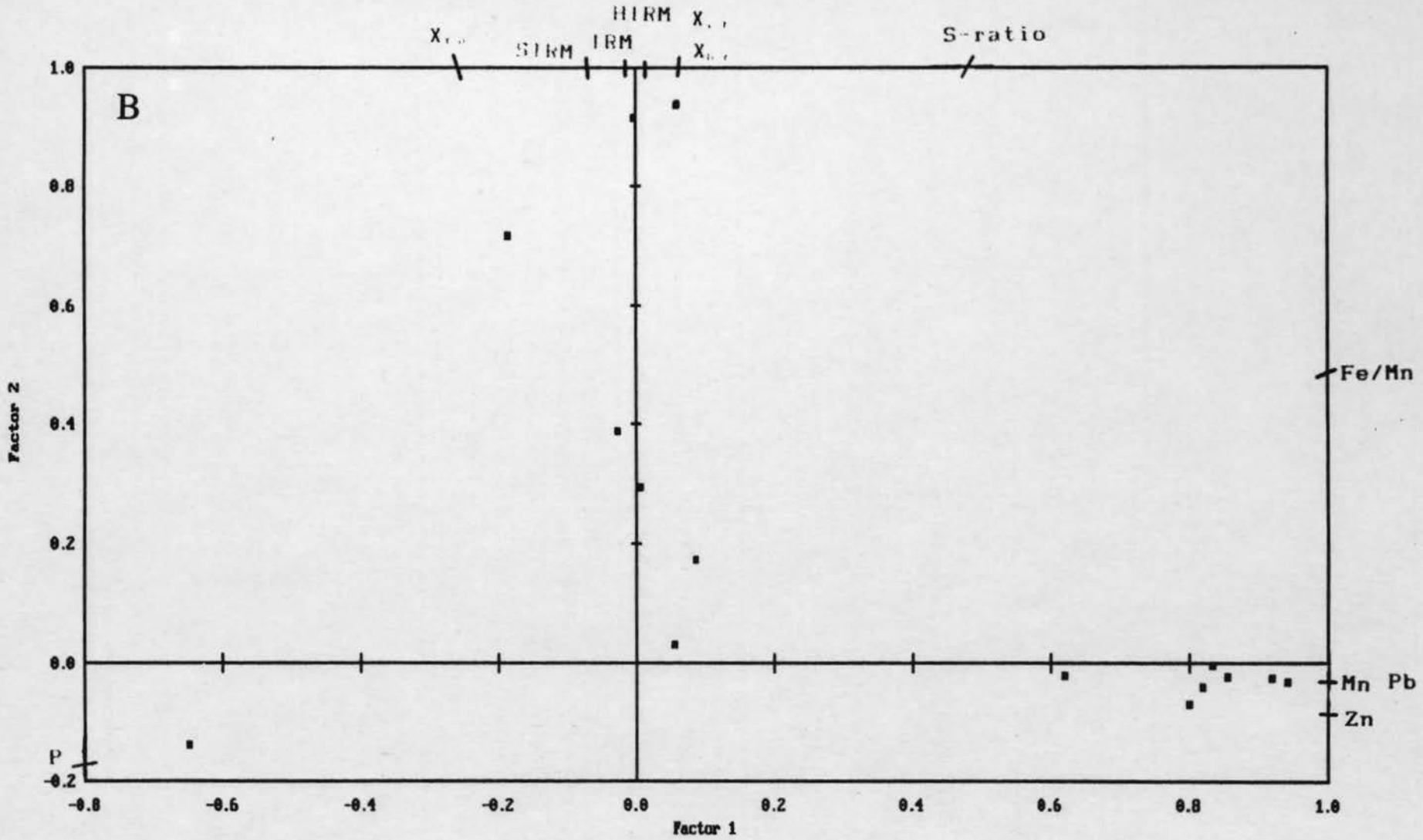
Factor	Eigenvalue	Pct of Var	Cum Pct
1	8.11116	50.7	50.7
2	2.46384	15.4	66.1
3	1.81849	11.4	77.5
4	1.12263	7.0	84.5
5	.82735	5.2	89.6
6	.60056	3.8	93.4
7	.39789	2.5	95.9
8	.31720	2.0	97.9
9	.19907	1.2	99.1
10	.06731	.4	99.5
11	.03555	.2	99.8
12	.01733	.1	99.9
13	.01537	.1	100.0
14	.00392	.0	100.0
15	.00234	.0	100.0
16	.00000	.0	100.0

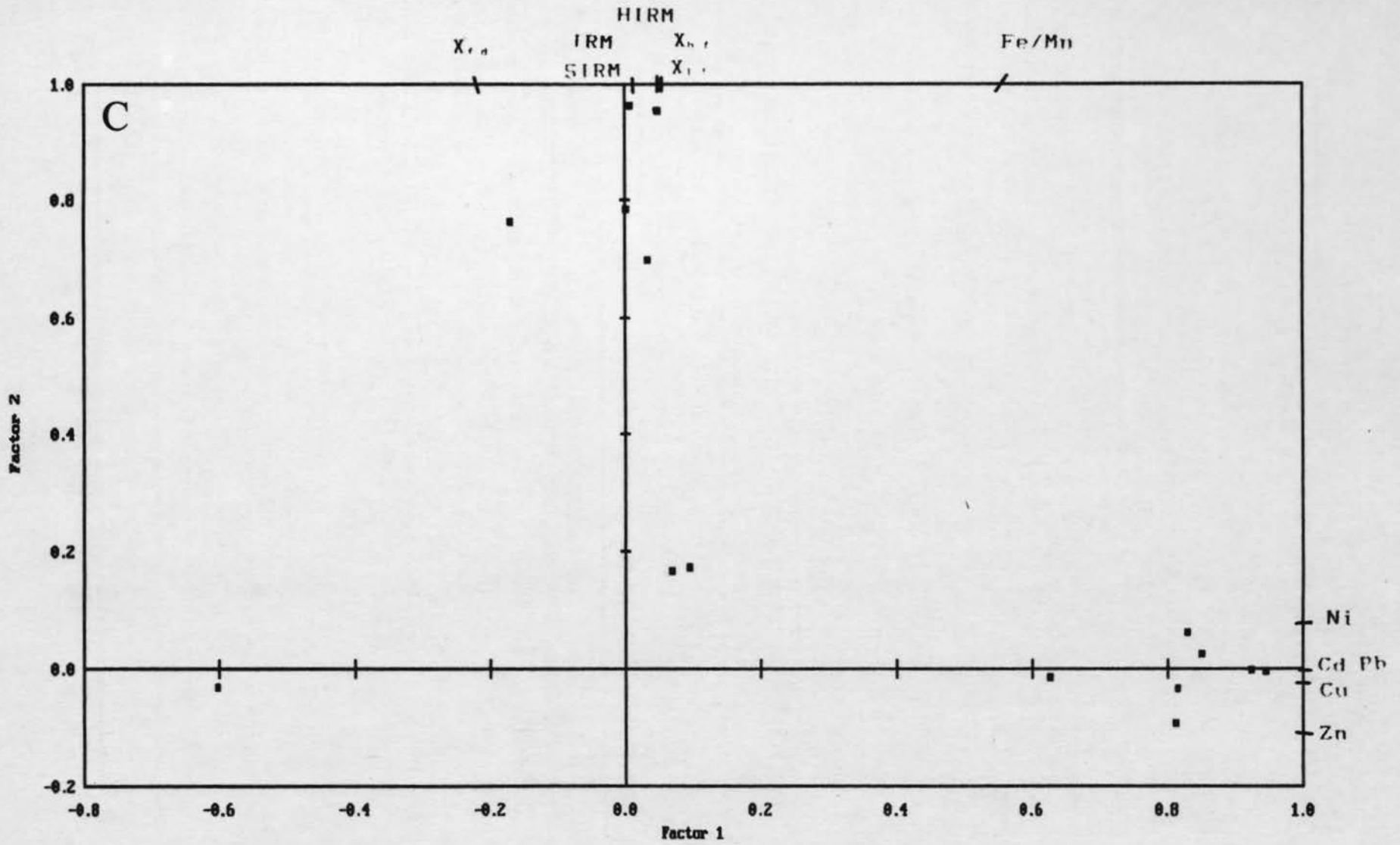


Factor	Eigenvalue	Pct of Var	Cum Pct
1	6.17183	38.6	38.6
2	4.56537	28.5	67.1
3	2.03769	12.7	79.8
4	1.08044	6.8	86.6
5	.69602	4.4	90.9
6	.65966	4.1	95.1
7	.22665	1.4	96.5
8	.16593	1.0	97.5
9	.13967	.9	98.4
10	.09714	.6	99.0
11	.08267	.5	99.5
12	.06666	.4	99.9
13	.00838	.1	100.0
14	.00183	.0	100.0
15	.00005	.0	100.0
16	.00000	.0	100.0

Fig 5.23 Rotated factor plots
a. core A0
b. core B0
c. core C0
d. core D0




B
HIRM
SIRM
IRM
S-ratio
Fe/Mn
Mn
Pb
Zn
P
Factor 2
Factor 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0


C
HIRM
IRM
SIRM
Fe/Mn
Ni
Cd Pb
Cu
Zn
Factor 2
Factor 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0

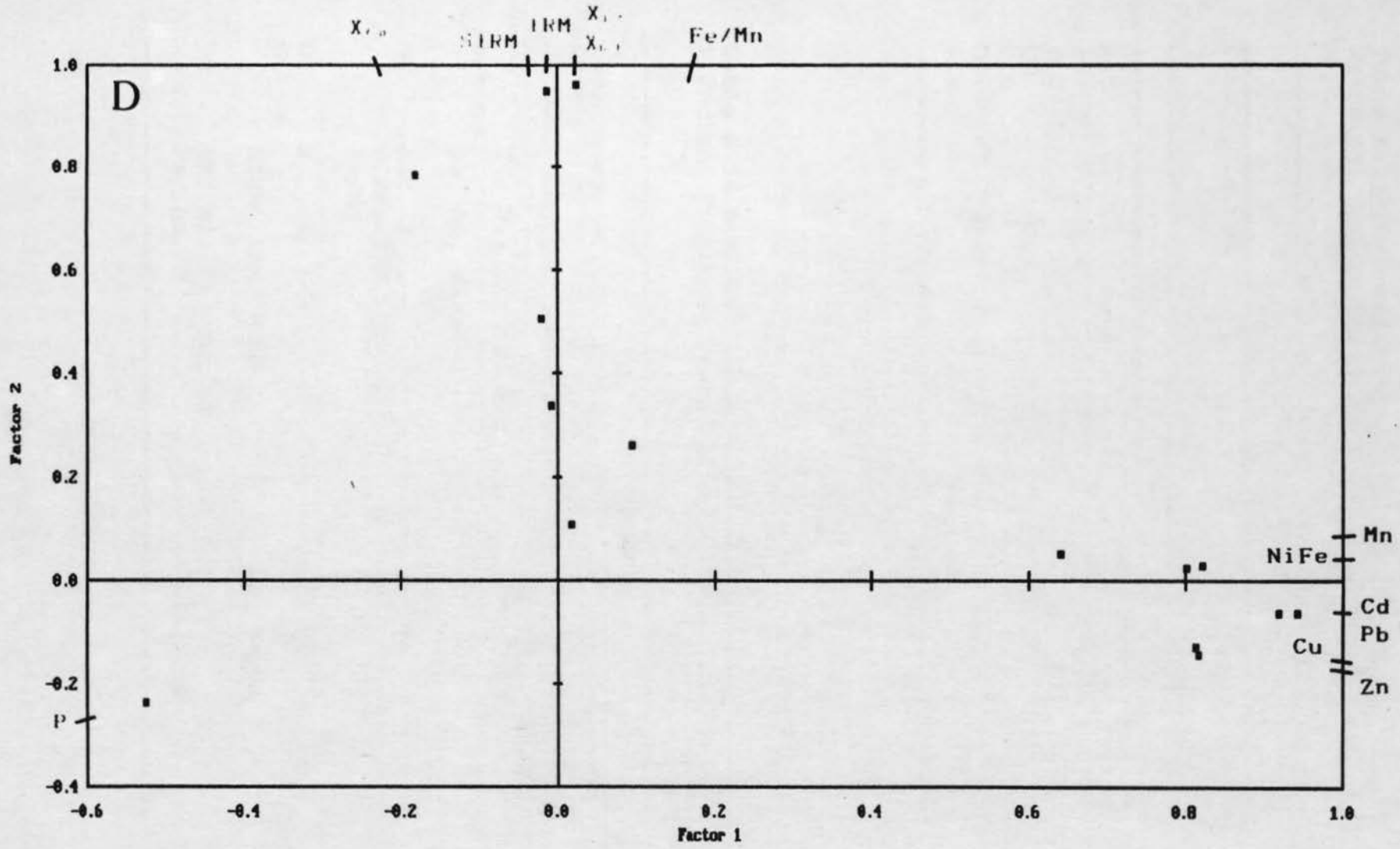

D
SIRM
IRM
Fe/Mn
Mn
NiFe
Cd
Pb
Cu
Zn
P
Factor 2
Factor 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0

Table 5.13 Percentage explained variance of Principal Components in Wyken Pool lake cores

	Factor		
Core 4	1	2	3
AO 4.1	57.6	15.4	12.9
BO 6.0	33.0	27.1	15.6
CO 7.0	50.7	15.4	11.4
DO 6.8	38.6	28.5	12.7

Table 5.14 Dominant parameters identified by Principal Component Analysis in factors 1 and 2

	Factor	
Core	1	2
AO	X_{lf}, X_{hf}, X_{fd} Cd, Ni, Pb, Zn, Cu Fe, Mn, Fe/Mn	X_{lf}, X_{hf}, SIRM, IRM, HIRM, S-ratio
BO	Xlf, X_{hf}, SIRM, IRM, HIRM Fe/Mn	Zn, Pb Mn
CO	X_{lf}, X_{hf}, X_{fd}, SIRM, IRM, HIRM	Cd, Ni, Pb, Cu, Zn Mn, Fe/Mn
DO	Cd, Ni, Pb, Cu, Zn Fe, Mn, P	X_{lf}, X_{hf}, X_{fd}, SIRM, IRM

level of correlation are indicated on these plots, unlabelled points represent variables which do not appear to be significant. These plots emphasise the lack of any relationship between heavy metals and magnetic characteristics in the lake cores with the heavy metals mainly clustered along the positive X axis, and the mineral magnetic parameters mainly clustered along the positive Y axis.

5.4 Summary

Wyken Pool is a shallow, freshwater lake which contains up to 1m of sediment which infills a shallow depression caused by mining subsidence in the mid-nineteenth century. At an average depth of 47 cm in the sediment column there is a transition to dry, friable soil which probably represents the original land surface before subsidence. In general, the lake sediment, a black, organic gyttja, is deepest along the eastern side of the lake and shallowest long the western side. The exact date of the transition from soil to lake sediment is not supported by the amount of documentary evidence found for Swanswell Pool. However, the presence of *Dreissena polymorpha*, the Zebra Mussel, just above the soil in the core by the outlet gives an earliest date of about 1850.

Many of the analyses, such as bulk density, heavy metal concentration and mineral magnetic measurements indicate changing sedimentation, particularly in the cores nearest the inlets, in the middle third of the lake sediment core. This is manifest by higher dry bulk density, lower heavy metal concentration and lower mineral magnetic measurements. Dating

using ^{137}Cs suggests that there may be a slightly higher sediment accumulation rate pre-1954, commensurate with the building of residential housing in the catchment during the post-war period. These levels of sediment flux may have been maintained until the late 1970s and hence the ^{137}Cs 1954 marker horizon lies within the lake sediments with higher density and lower concentration of heavy metals in the central third of the core. The peak in ^{137}Cs activity corresponds well to 1963 using the average sediment accumulation rate of 0.54 cm yr^{-1}, but further work is needed to confirm these data, which are based on the incomplete measurement of one core.

The flux of ^{210}Pb to the sediments was too low to allow accurate dating using this isotope, but comparison of the ratios of supported : unsupported ^{210}Pb in the upper sediment of Wyken Pool with those of Swanswell Pool, rural and remote rural sites showed that there was a gradient in activities in which the highest proportion of unsupported ^{210}Pb was found in the city centre site at Swanswell Pool, followed by Wyken Pool, Merevale Lake and Seeswood Pool.

Mineral magnetic properties indicate the dominance of particulate pollutants in the sediments but that the source of the magnetic minerals has not changed during the deposition of the gyttja.

The upper sediments in the lake cores show elevated heavy metal concentrations, possibly from industry and urbanisation, with the profile divided into two further zones; one of gradually decreasing concentration in the middle of the core and then low concentrations representing the oldest sediments

at the base of the core. Non-metallic elements markedly reflect this three-fold trend in sedimentation.

The statistical analysis of the grid of cores from Wyken Pool has shown that there is considerable intercorrelation between the magnetic parameters and also between the individual heavy metals. The correlation between heavy metals and magnetic parameters is inconsistent, regression suggesting that mineral magnetic characteristics would not provide a consistent surrogate for heavy metal measurement in Wyken Pool. PCA is inconclusive, with heavy metals dominating factor 1 in some cores and magnetic parameters dominating in others. PCA reflects a mixture of factors contributing to the characteristics of a complex system in which the scale of anthropogenic influence is neither consistent nor predictable.

Comparison with Swanswell Pool shows that both lakes are significantly enriched in heavy metals in comparison with background concentrations, and in comparison with other published values of F, are particularly enriched in Zn.

Chapter 6 outlines the results obtained from analysis of the catchment components in the Wyken Slough system. A combination of the results from both the lake and the catchment provide the basis for the discussion in Chapter 7 in which a comparison is made between the closed Swanswell Pool and the open Wyken Pool and an assessment made of the relative contribution of the catchment to the lake sediment heavy metal record.

Chapter 6

The Wyken Pool catchment

6.1 Introduction

This chapter presents the results of physical and chemical analyses of samples taken from the catchment surrounding Wyken Pool. Chapter 3.4.2 discussed the derivation of naming the area "Wyken Slough", showing that the term "Slough" was from a Medieval word meaning "marsh". To differentiate between analysis undertaken in Wyken Pool itself, the term "Wyken Slough" has been adopted to refer to inflowing and outflowing streams, the soil, the marsh, stream and lake water associated with the catchment of Wyken Pool. These 4 parts of Wyken Slough will be referred to as the catchment components. Table 2.21 lists the analysis carried out on the catchment components at Wyken Slough and Tables 2.16 b and 2.19 list the samples taken in order to:

1. Establish the spatial and vertical distribution of various characteristics of the sediment in the marsh. From this to establish the capacity of the marsh as a sink for heavy metals and hence the role it may have in controlling heavy metal delivery to Wyken Pool.

2. Establish the distribution of various characteristics of the bed sediments in the inflowing and outflowing streams. From this to attempt to differentiate between sources within the fluvial system and to estimate the capacity of the stream bed sediments as a sink of heavy metals.

3. Establish the vertical distribution of various characteristics in the soils within the catchment. From this to estimate the atmospheric flux of heavy metals to the catchment.

4. Establish the quality of the water flowing into Wyken Pool, from this to assess the likelihood of remobilisation of heavy metals from the sediment sinks established in 1 and 2 above.

These data will be used in Chapter 7, in association with results presented in Chapter 5, to calculate heavy metal and sediment budgets for Wyken Pool.

In order to carry out the above, a variety of analyses were carried out on the catchment components of Wyken Slough. The parameters common to the solid samples included bulk density, total heavy metals analysis, mineral magnetic measurements and P, Fe and Mn concentrations. P, Fe and Mn are considered separately in their role as indicators of nutrient and redox status respectively. The use of the analyses to characterise or fingerprint deposits were discussed in Chapter 2.10. In the case of mineral magnetic measurements, these were

specifically used to characterise a deposit to enable the source of the sediment to the lake to be identified. The use of X_{lf} / SIRM scattergrams in sediment sourcing is discussed in more detail in Chapter 4.2.5 c and Chapter 2.10.ie.

Chapter 6 is structured around the catchment components introduced in points 1 - 4 above. These sections are further subdivided to discuss the individual analyses introduced above.

Section 6.5 subjects the analysis of the solid substrates to various statistical tests, the aims of which are covered in Chapter 2.13 and the theory is covered in Chapter 4.3. Water quality is discussed in section 6.6 and is used to assess prevailing environmental conditions as well as the stability of heavy metal sinks in the catchment. Section 6.7 summarises the results of analysis in the Wyken Slough and also gives a synthesis of the data from Swanswell and Wyken Pools which will be built upon in the overall discussion in Chapter 8.

6.2 The Wyken Slough marsh sediments

This section is divided into two subsections to consider the characteristics of the surface samples taken from the marsh and also the vertical profiles of 2 cores taken from the locations shown on Fig 2.11 a.

a. Surface spatial patterns

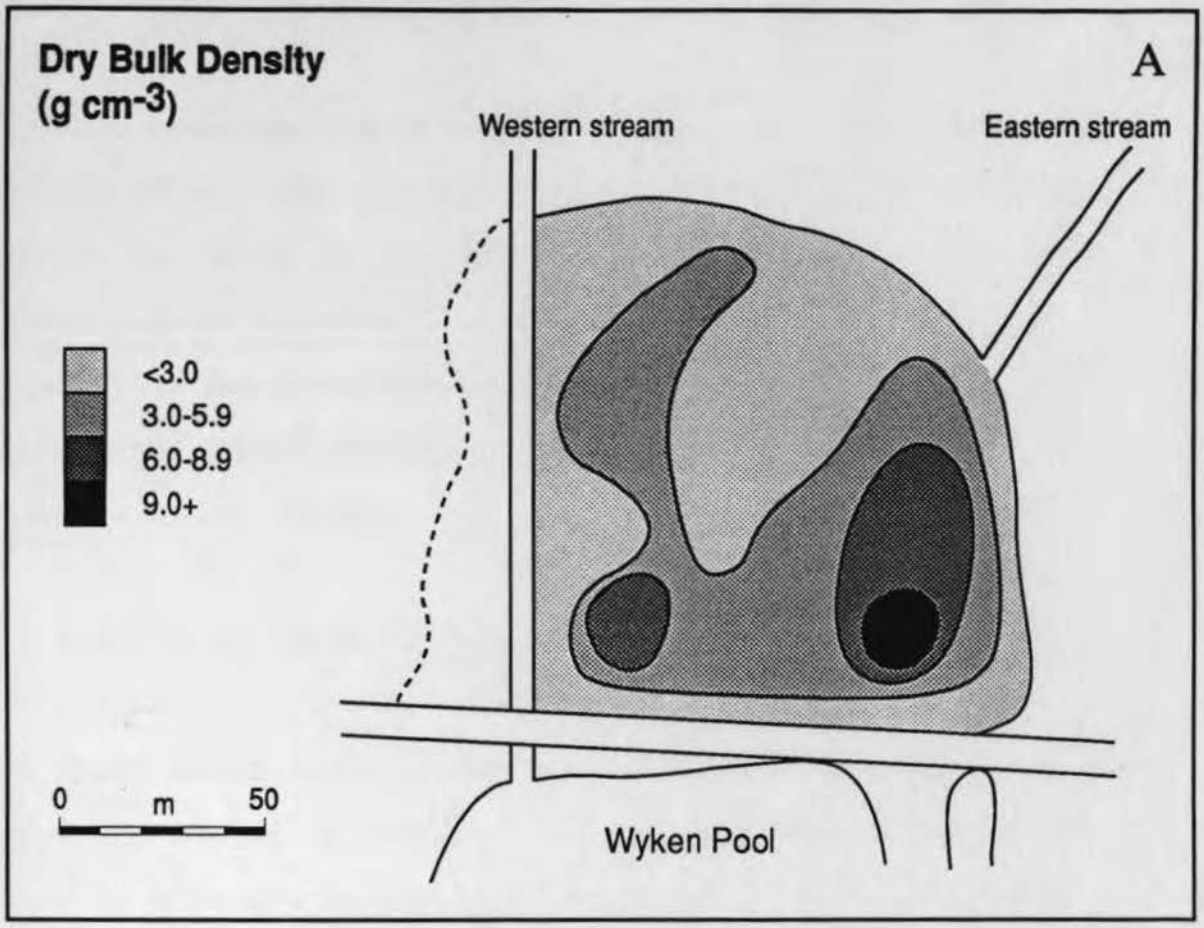
This subsection is further divided into four parts: bulk density, total heavy metals, mineral magnetic measurements and P, Fe and Mn. Their spatial distribution in the surface samples of the marsh are examined in order to ascertain whether such properties are evenly distributed or whether there are areas of net deposition or net erosion which may impact upon the quality of sediment which eventually passes through the marsh and into the lake.

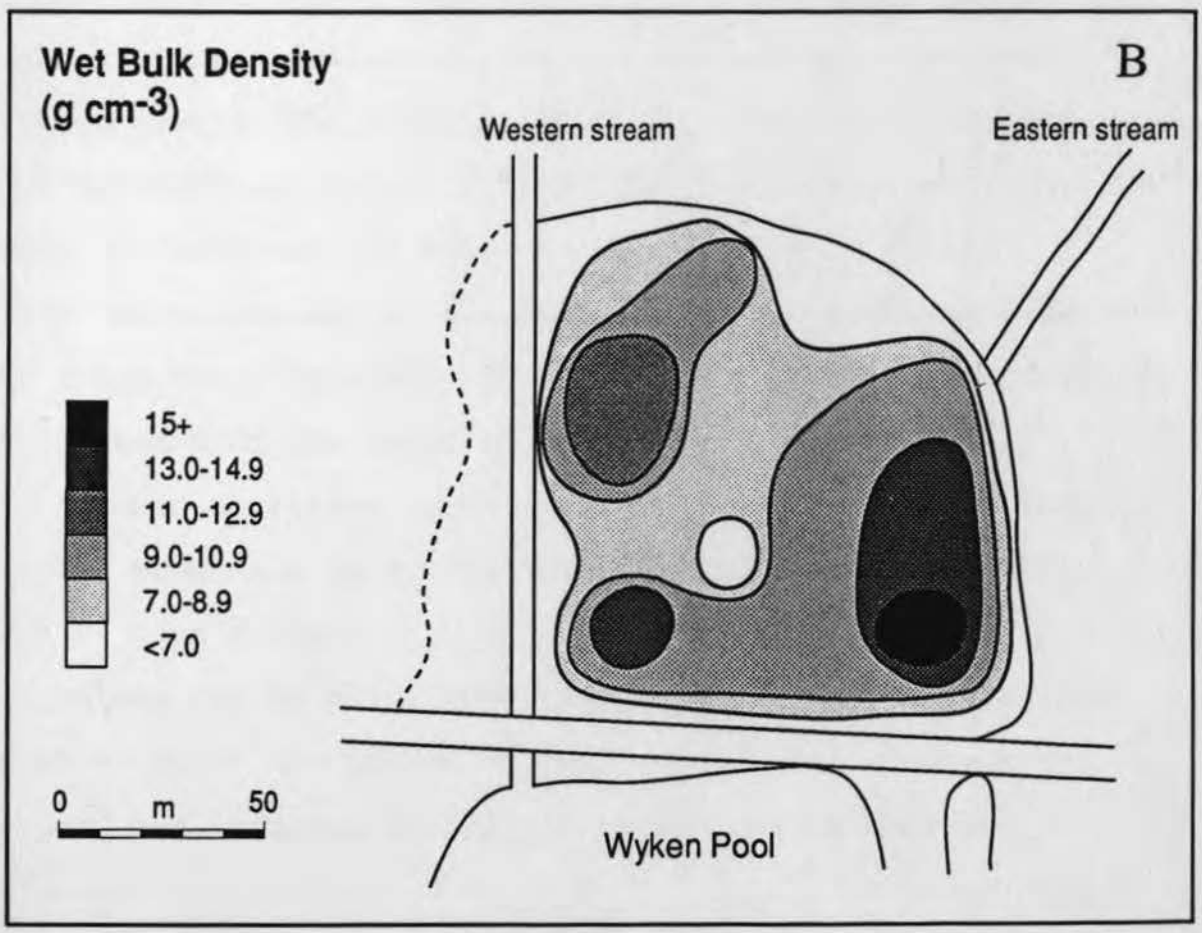
i. Bulk density

The wet and dry bulk densities of the upper 10cm of the marsh are contoured in Fig 6.1. Areas of higher dry bulk density are located in the eastern and western corners of the marsh with a central area of low density focusing on sample B4 (Fig 2.11 a). The distribution of values for wet bulk density, however, appear more complex as there are three areas of high density; in the northeastern, southwestern and southeastern areas. Sample B4 again has the lowest values.

Wet and dry bulk densities range from 15.4 g cm^{-3} and 9.7 g cm^{-3} respectively in the eastern corner of the marsh to 5.6 g cm^{-3} and 1.5 g cm^{-3} at B4 respectively. Both parameters tend to decrease around the edges of the marsh and to increase towards the outlet into the lake.

Fig 6.1 Spatial distribution of bulk density in the surface sediments of the marsh
a. Dry bulk density
b. Wet bulk density





The areas of highest bulk density are therefore associated with the eastern stream, in particular the area just to the north of the inlet to the lake. A further area of higher values is found in the southwestern corner of the marsh. This may have been associated with the western stream before its' improvement in the 1970s by the cutting of the drainage ditch (Chapter 3.4.2).

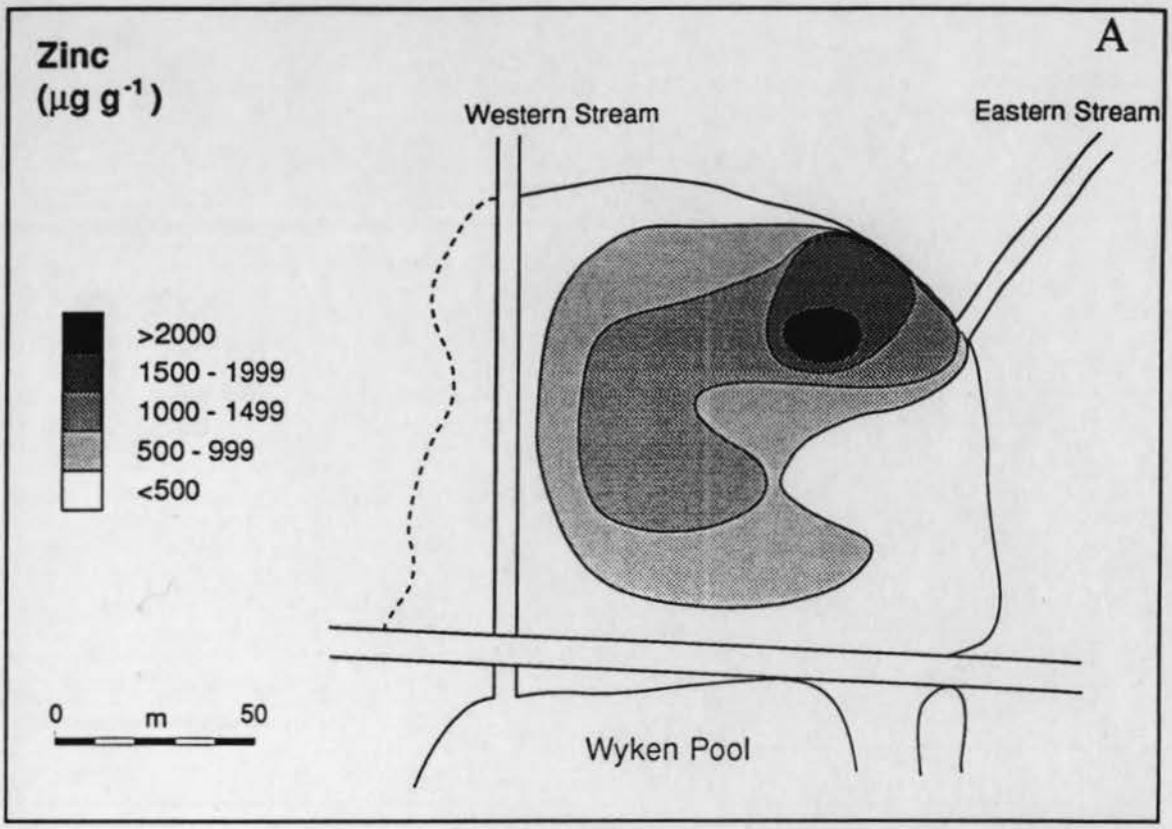
ii. Total heavy metal content of surface marsh sediments

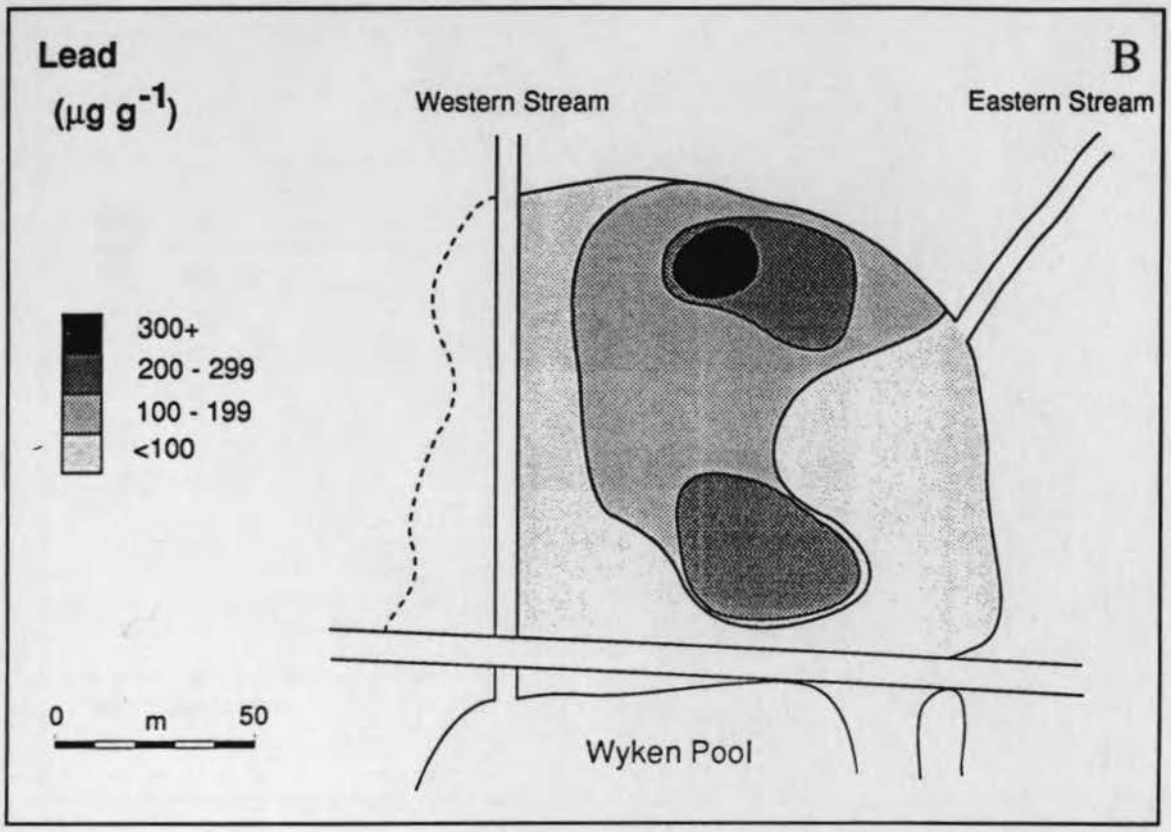
The heavy metal concentrations in the upper sediments of the marsh are mapped in Figs 6.2 a-c. In the case of Zn and Ni, there is a single sample (centred around the inlet of the eastern stream) where the concentrations of these metals are highest. Concentrations decrease in a regular, concentric pattern towards the inlet to the lake. Cu, Pb and Cd, however, have an additional area of high concentration situated in the south of the marsh. In the case of Cu, this is in the southwestern corner; in the case of Pb, it is midway between the A and the D transects (Fig 2.11) and in the case of Cd, it is located near the inlet to the lake.

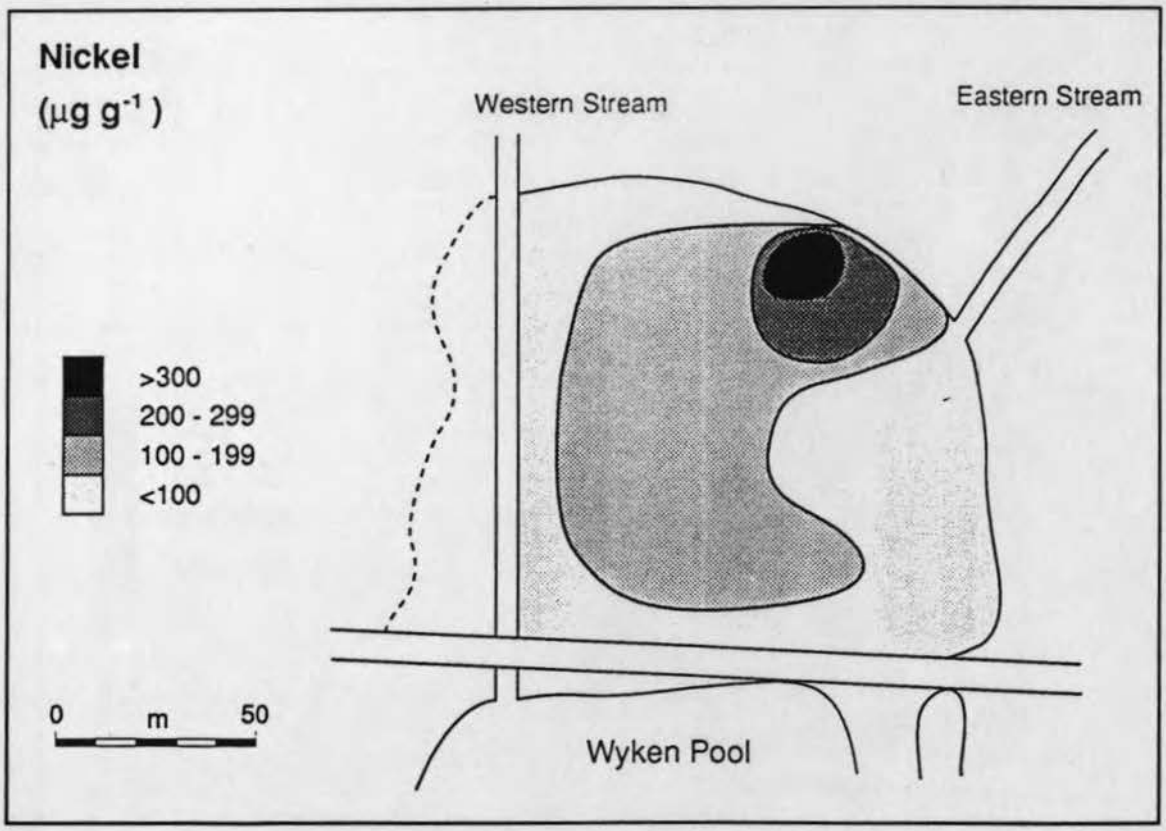
Cu concentrations tend to decrease towards the southeast, ranging from 46.8 $\mu g\ g^{-1}$ in the north to 2.9 $\mu g\ g^{-1}$ in the southeastern corner.

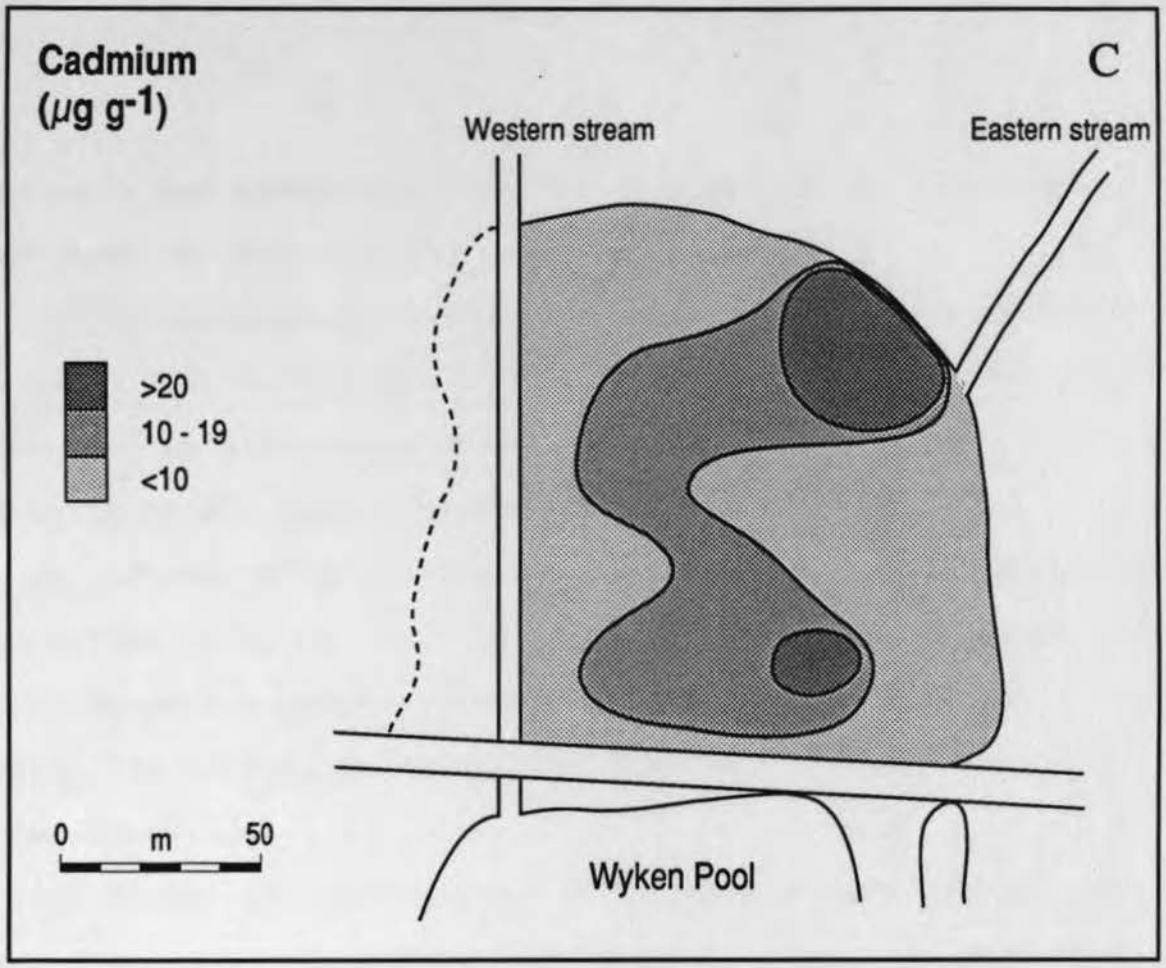
Values for Pb range from 324 $\mu g\ g^{-1}$ in the north of the marsh to below the limits of detection in the southeastern corner. The tendency is for concentrations to decrease

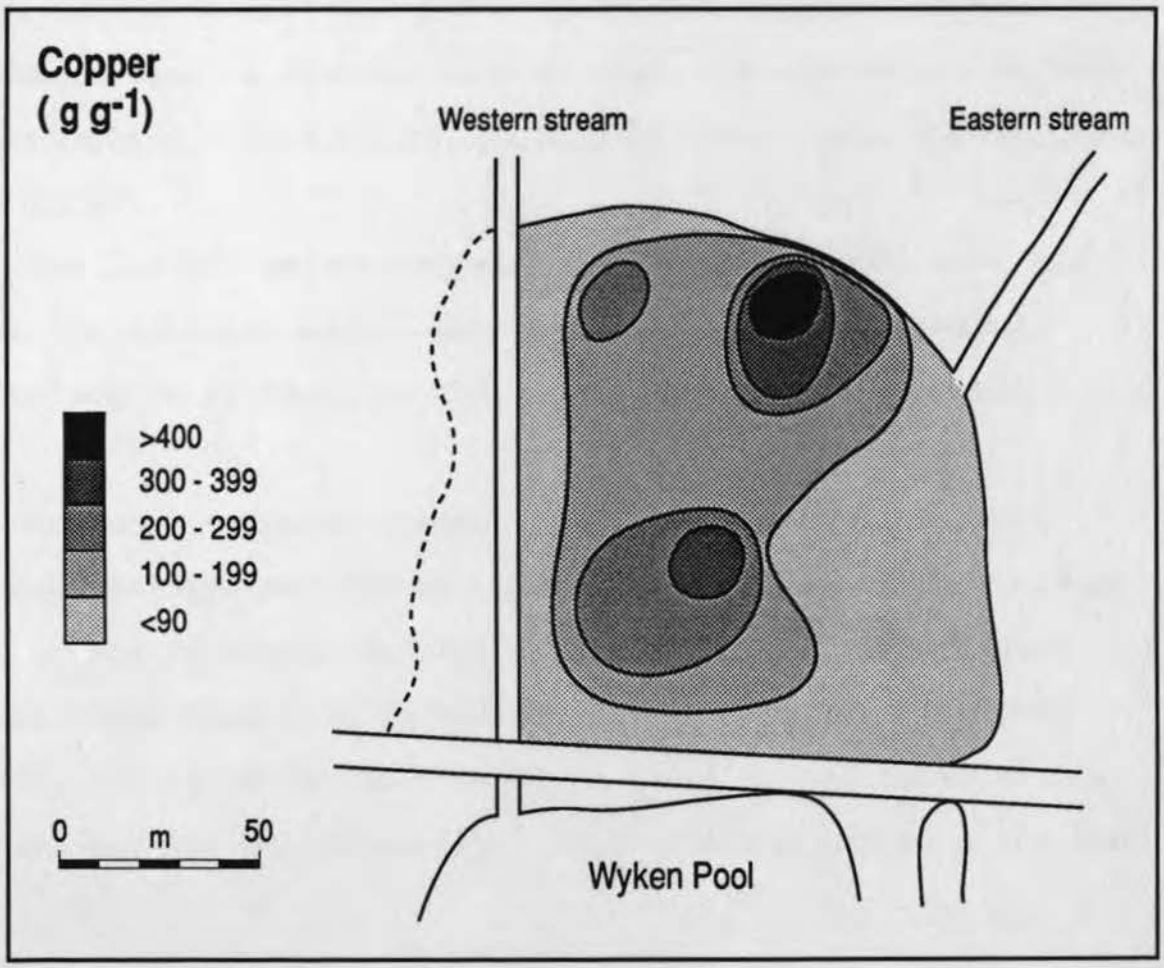
Fig 6.2 Spatial distribution of heavy metals in the surface sediments of the marsh
a. Zn
b. Pb and Ni
c. Cd and Cu




Lead
(µg g-1)
B
Western Stream
Eastern Stream
300+
200 - 299
100 - 199
<100
0
m
50
Wyken Pool


Nickel
(µg g-1)
Western Stream
Eastern Stream
>300
200 - 299
100 - 199
<100
0
m
50
Wyken Pool


Cadmium
(μg g-1)
C
Western stream
Eastern stream
>20
10 - 19
<10
0
m
50
Wyken Pool


Copper
(g g-1)
Western stream
Eastern stream
>400
300 - 399
200 - 299
100 - 199
<90
0
m
50
Wyken Pool

southwards and eastwards, with the highest values found in areas near the marsh outlet.

Zn tends to be concentrated in the northeastern area of the marsh with values decreasing southwards and eastwards in a concentric pattern. Concentrations range from 2178 $\mu g\ g^{-1}$ in the north to 275 $\mu g\ g^{-1}$ in the southeast.

The pattern of Ni concentration parallels that of Zn, with high values of up to 306.3 $\mu g\ g^{-1}$ in the north to 47 $\mu g\ g^{-1}$ in the southeastern corner. Concentrations tend to decrease towards the outlet, in particular towards the eastern margin of the marsh.

The higher Cd values appear in a central band through the marsh from north to south. Concentrations vary from 28.7 $\mu g\ g^{-1}$ in the north near the inlet, to a minimum east of the outlet. There is also an area of lower concentrations in the northwestern corner of the marsh, and here levels remain above 5.9 $\mu g\ g^{-1}$.

Two factors associated with the history of the site and with its function as a marsh could influence the spatial distribution of heavy metals in the surface of the marsh:

1. Chapter 3.4.2 showed that since the 1970s, the western stream has bypassed the marsh in a deep, steep-sided drainage ditch, and fluvially derived source of heavy metals to the marsh since that time should therefore be from the eastern inlet. The accumulation rate of sediment in the marsh is not known, but the bulked samples taken from the top 10 cm of the

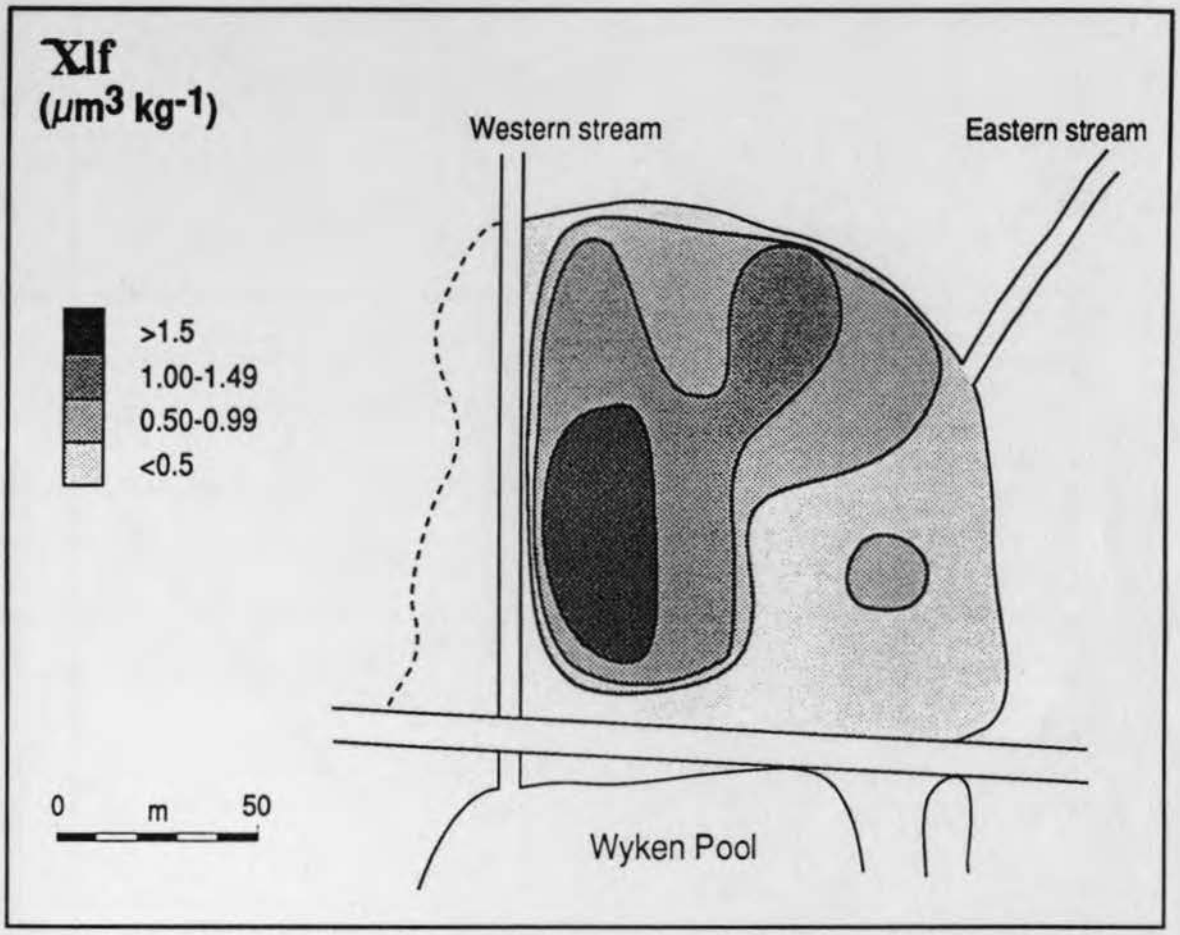
marsh still may retain the record of when the western stream used to percolate through it when passing into the lake. This is manifest in an area of slightly higher heavy metal concentrations along the western side of the marsh.

2. The route of water flow through the marsh is unknown although marshes, or "riverine wetlands" (Orme, 1990, p77) are characterised by low gradients and hence slack flows, leading to the development of meandering multiple channels. The distribution of heavy metals and bulk density may therefore reflect the breaking up of the stream into sinuous channels and the deposition of sediment as the stream energy falls upon entering the marsh. Future work could therefore include an examination of the pathway of the stream through the marsh and an application of the spatial patterns of heavy metal concentration to the analysis of flow. This would show how the water percolates through the marsh and how permanent or ephemeral the channels are. This would give information on whether contaminated sediment could be deposited over the whole marsh over time.

iii. Mineral magnetic measurements

χ_{lf} and SIRM (Figure 6.3) exhibit the same broad distribution across the surface sediments of the marsh. There is one significant area of high values which occurs along the western edge where χ_{lf} reaches 1.87 μm^3 kg^{-1} and SIRM reaches 28 mAm^2

Fig 6.3 Spatial distribution of mineral magnetics parameters in the surface sediments of the marsh, χ_{lf} and SIRM



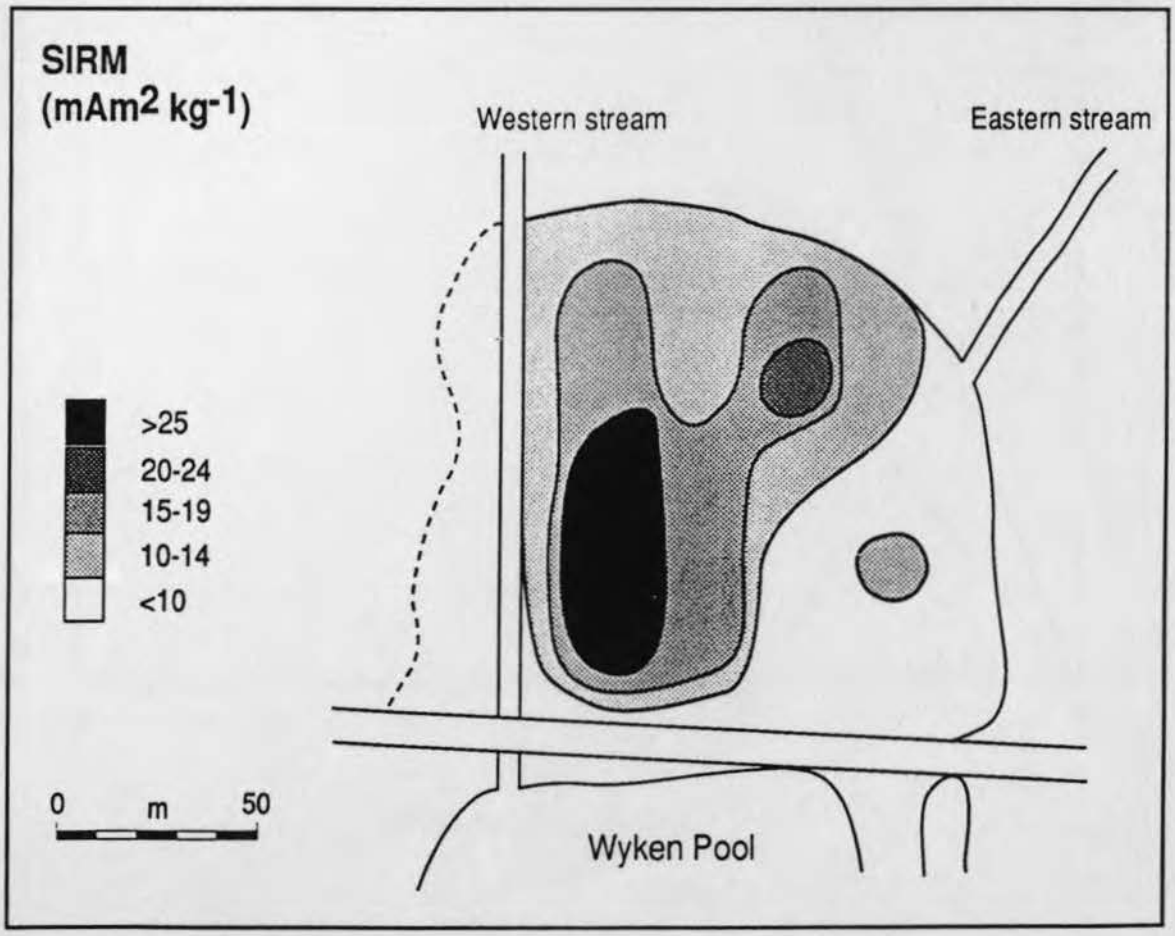
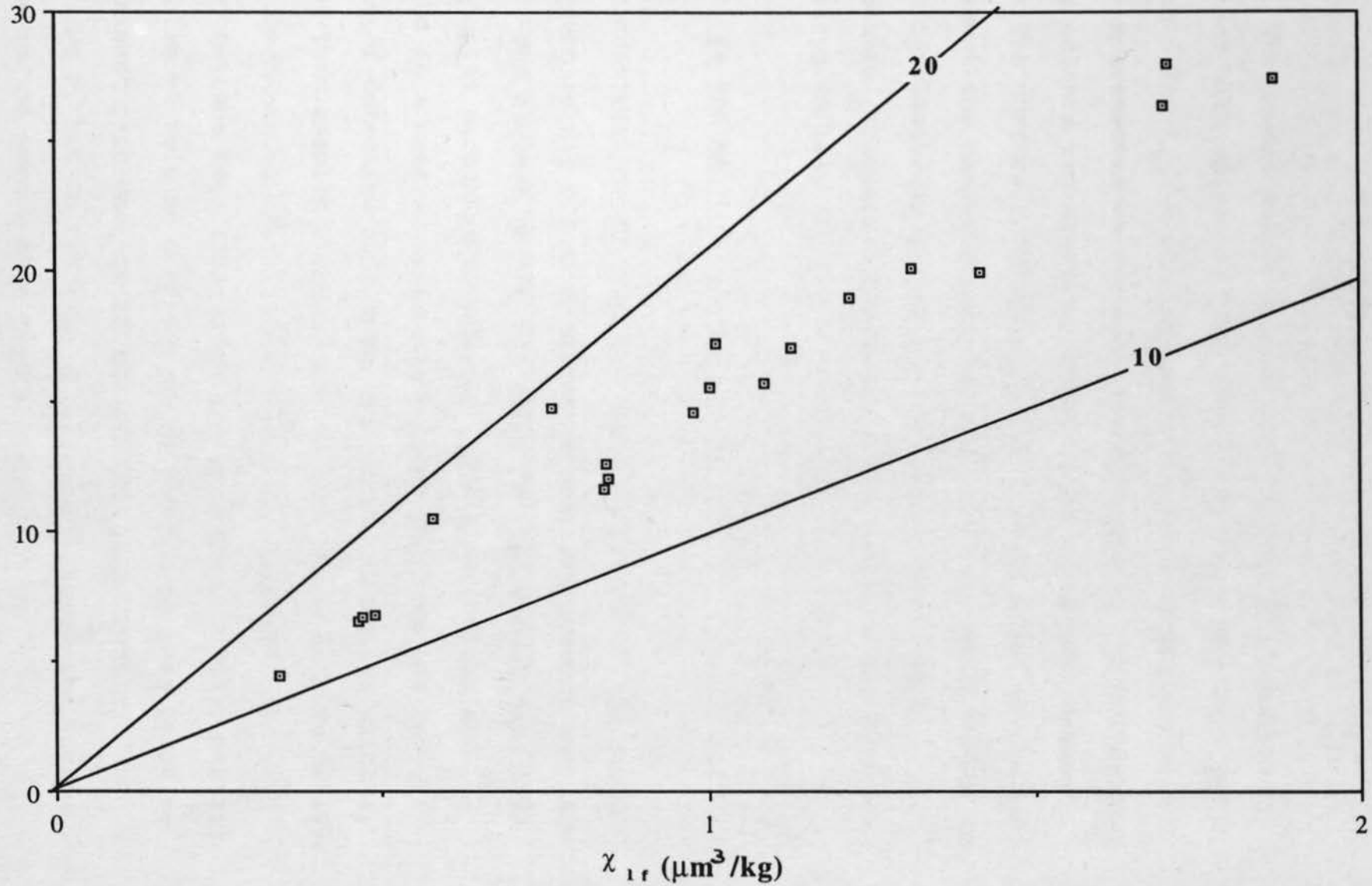


Fig 6.4 Scattergram of χ_{lf} against SIRM for marsh surface samples

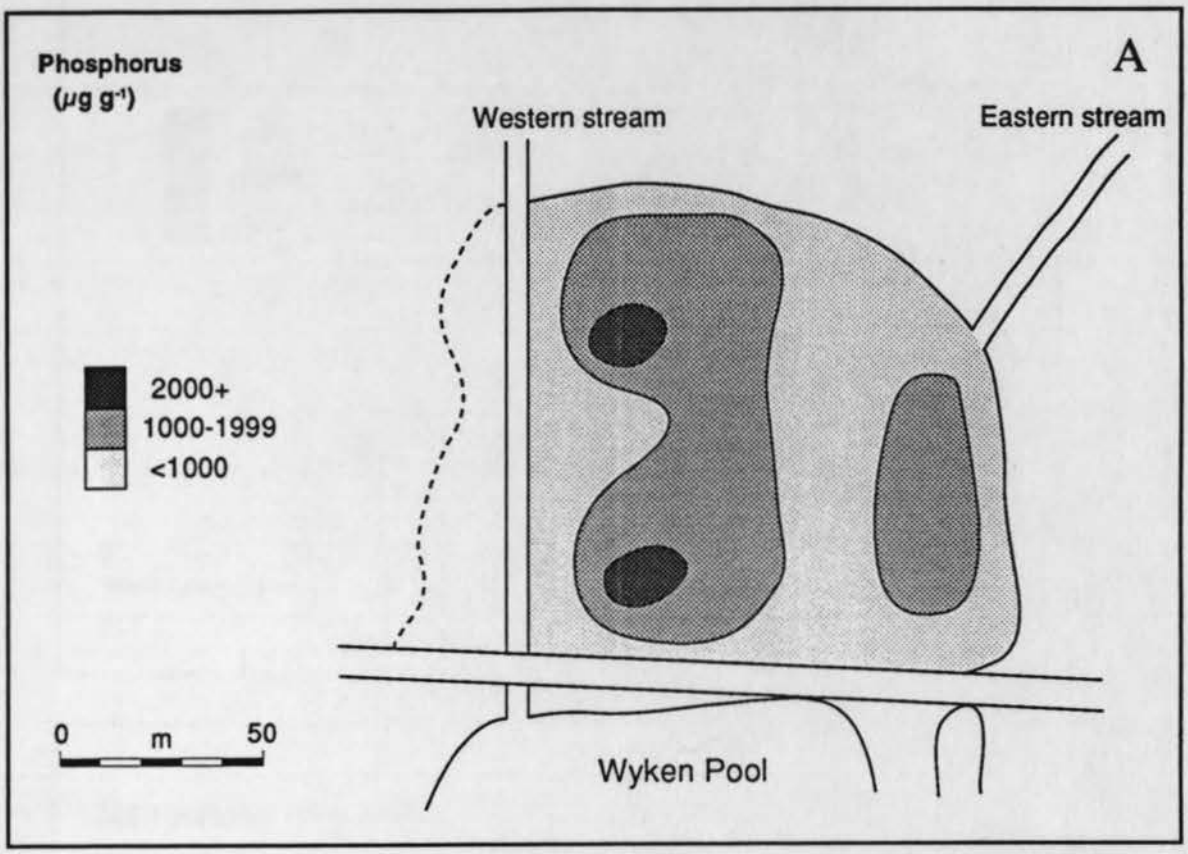


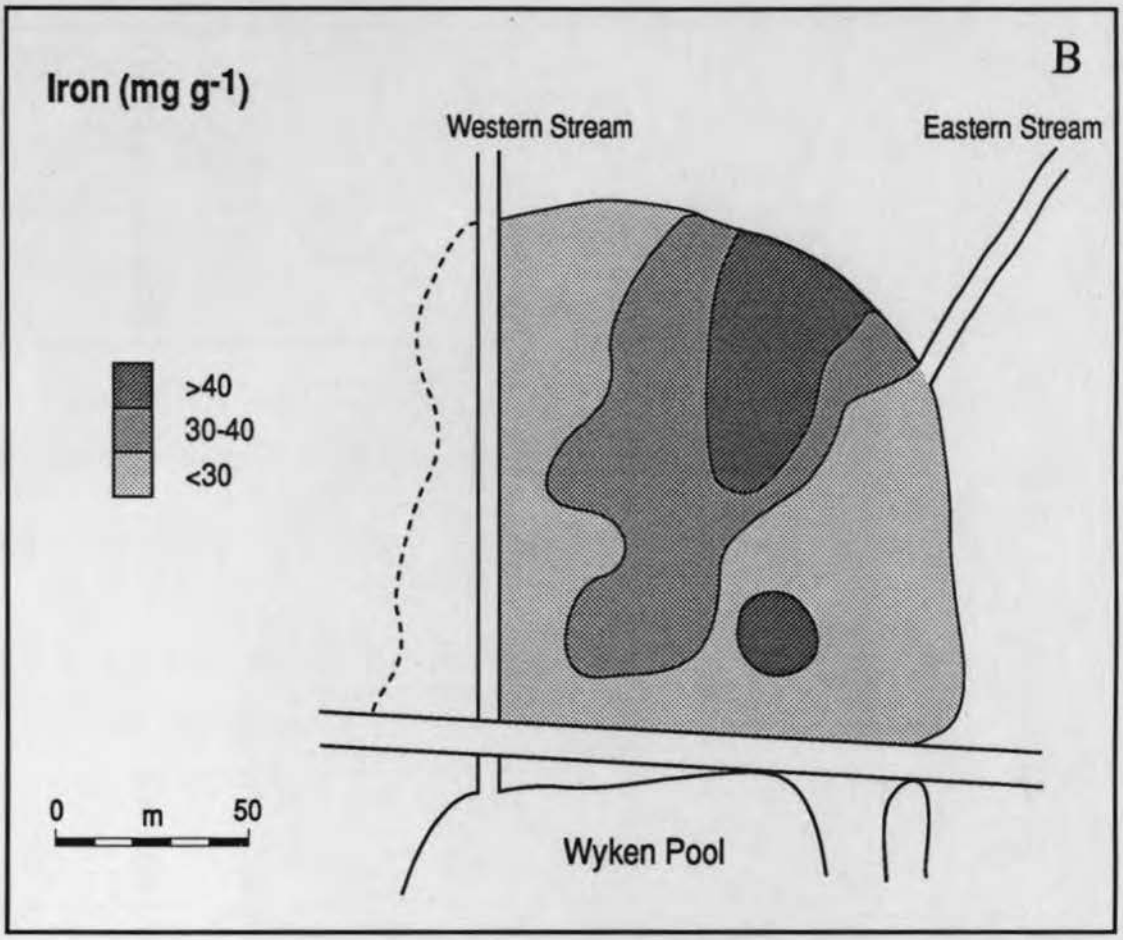
kg^{-1}. The lowest values are recorded in the southeastern quadrant with values of less than 5 mAm^2 kg^{-1} for SIRM and 0.5 μm^3 kg^{-1} for χ_{lf}. A scattergram of χ_{lf} with SIRM for these data is presented in Fig 6.4. Superimposed on the scattergram are gradients representing ratios of 10:1 and 20:1 between which the surface marsh samples fall. These lines of gradient represent the characteristic mineral magnetic characteristics of MD ferrimagnetic grains such as particulate bound pollutants (Thompson & Oldfield, 1986. See also Fig 4.16 and Chapter 2.10 ie).

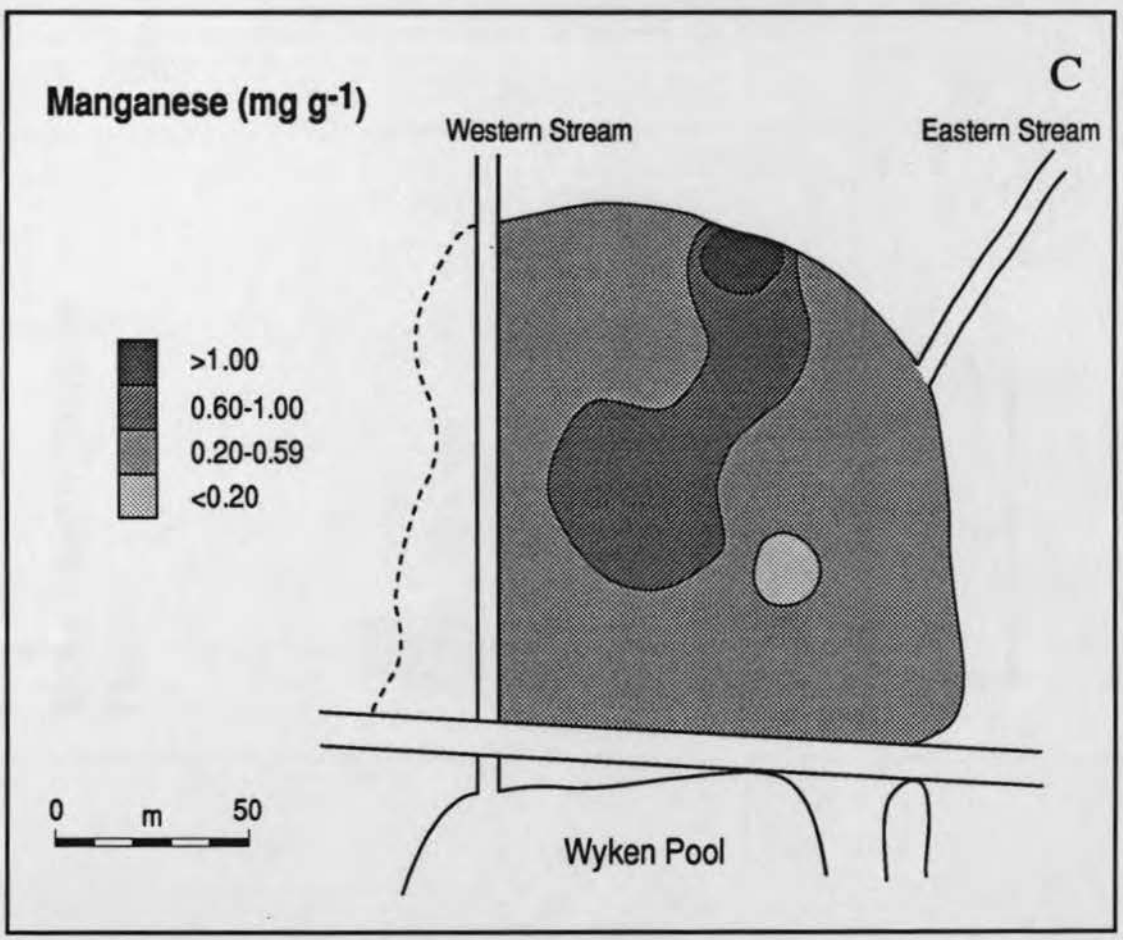
iv. P, Fe and Mn

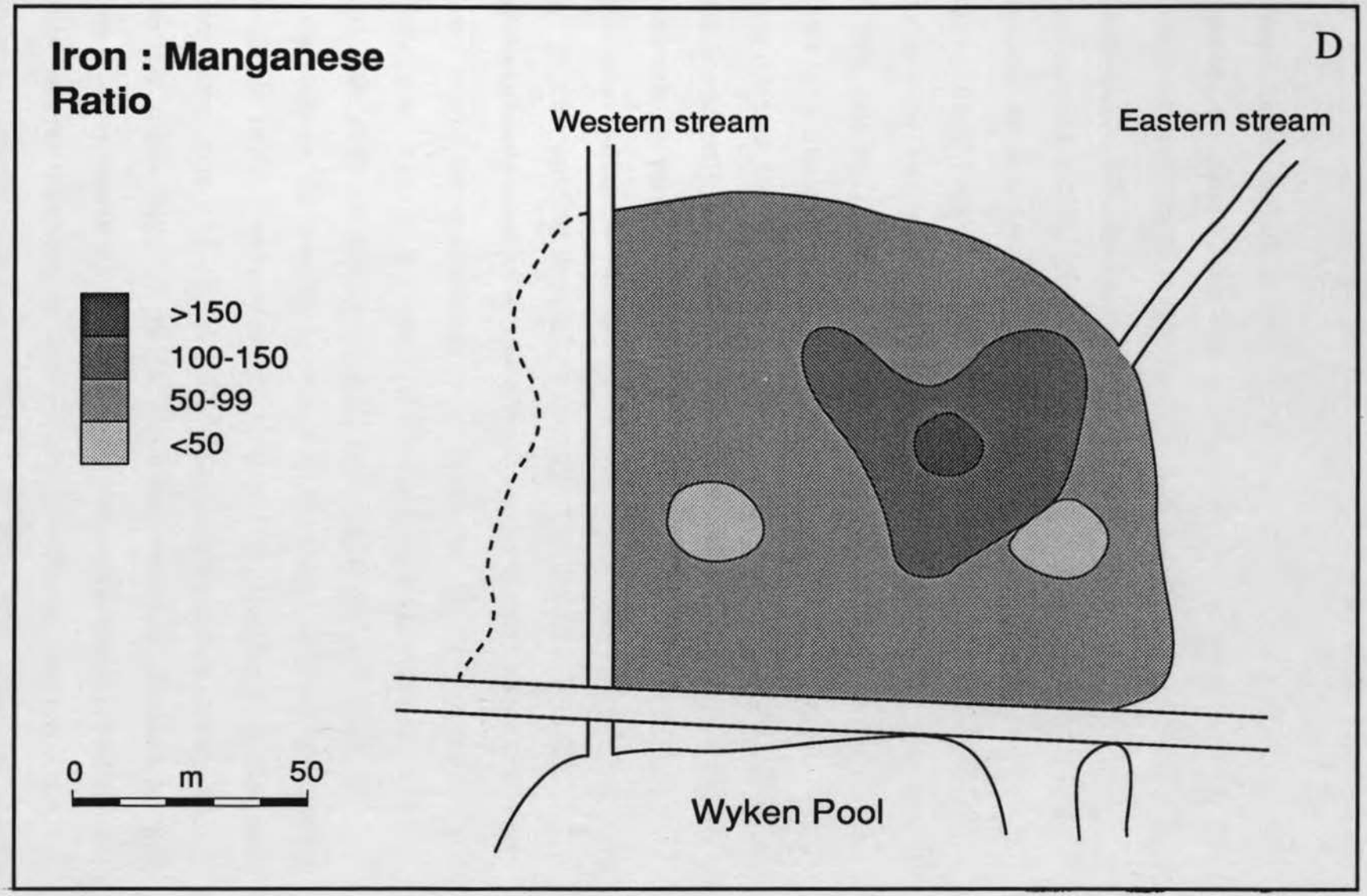
The concentrations of P in the upper sediments of the marsh are given in Fig 6.5 a. P values do not vary greatly over the marsh. The highest values are found in the western half with two samples exceeding 2000 μg g^{-1}. The lower values are located in a central north-south band, reaching the lower limits of detection in places. The values found are slightly higher than results reported for Rattray Marsh on Lake Ontario by Glooschenko *et al.*, (1981), where the highest concentrations were 1227 μg g^{-1}. As Williams, (1990), states, the foremost role of a marsh, or wetland in an area prone to contaminant problems, is in the removal of pollution, including P, but in the case of P removal, there are finite limits on the amount that can be removed.

Fig 6.5 Spatial distribution of P, Fe, Mn and Fe / Mn in surface marsh sediments
a. P
b. Fe
c. Mn
d. Fe / Mn




B
Iron (mg g-1)
Western Stream
Eastern Stream
>40
30-40
<30
0
m
50
Wyken Pool


C
Manganese (mg g-1)
Western Stream
Eastern Stream
>1.00
0.60-1.00
0.20-0.59
<0.20
0
m
50
Wyken Pool


Iron : Manganese Ratio
D
Western stream
Eastern stream
>150
100-150
50-99
<50
0
m
50
Wyken Pool

The distribution of Fe and Mn in the surface samples of the marsh are shown in Figs 6.5 b and c. The highest values for each element are found in the north eastern quadrant of the marsh, to the north of the eastern stream. The lowest values are found in the sediments at the margins with the exception of one low Mn concentration located above the eastern inlet to the lake. The Fe / Mn ratio indicates that there may be two areas of reducing conditions, one associated with the low Mn / high Fe concentration and a second to the west of it. The highest ratios are found to the east of the centre of the marsh. This area may represent relatively more oxidising conditions and may be associated with the pathway of the stream through the marsh. Relatively more oxidising conditions would be found associated with the aerated running water of the active streams flowing through the marsh. Relatively more reducing conditions, and hence lower Fe / Mn ratios, would be associated with areas of still water (Mitsch & Gosselink, 1993). A high organic matter content could be associated with reducing conditions since degradation of organic matter is accompanied by high oxygen demand (Mitsch & Gosselink, 1993). Unfortunately, there are no spatial organic matter data, but Fig 6.6 c shows the profile for organic matter in marsh core 1. The highest percentage organic matter is found at a depth of 8 cm and is over 20% indicating that organic matter content of the marsh sediments may be high which would explain areas of low Fe / Mn ratio associated with reducing conditions.

b. Marsh sediment cores

This subsection is further divided into four parts considering bulk density and loss on ignition, total heavy metals, mineral magnetic measurements and P, Fe and Mn. Descriptions of the sediments in the marsh can be found in Appendix 3.

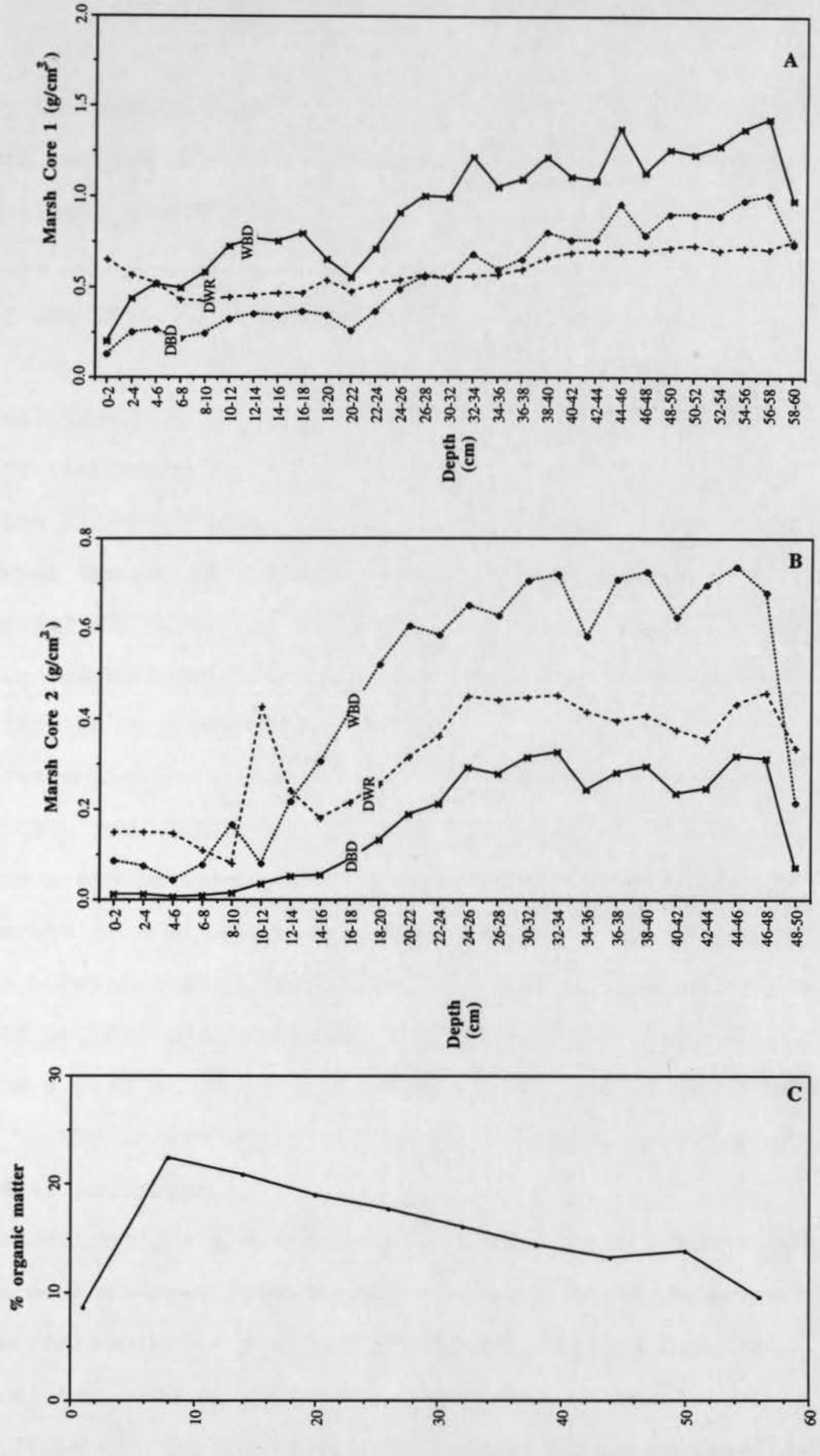
i. Bulk density and loss on ignition

The bulk density gradually increases with depth in both cores (Figs 6.6 a and b). There is a decrease in both wet and dry density in core 1 at 11 cm, and both parameters in both cores exhibit a marked drop in density in the basal sample. The values obtained for core 1 were generally higher than those for core 2. Values for wet bulk density in cores 1 and 2 ranged from 0.2 to 1.4 g cm^{-3} and 0.09 to 0.74 g cm^{-3} respectively. Those for dry bulk density for cores 1 and 2 ranged from 0.13 to 1.0 g cm^{-3} and 0.01 to 0.32 g cm^{-3} respectively.

Loss on ignition was measured on core 1 and is shown in Fig 6.6 c. Organic matter increases from 8% in the top sample to 22% at 8 cm. Below 8 cm depth, the general trend was for a gradual decrease in organic matter with increasing depth.

Low bulk density reflects high organic matter in the upper samples of both marsh cores. Primary productivity in marshlands is enormous (Williams, 1990) and can exceed that of grassland by between two and five times. The trend of

Fig 6.6 Downcore trends in bulk density and organic matter in marsh sediment cores a. Marsh core 1, bulk density b. Marsh core 2, bulk density c. % organic matter, both cores



gradually decreasing values of organic matter and bulk density with depth reflect the compression of sediments as overlying material slowly accumulates.

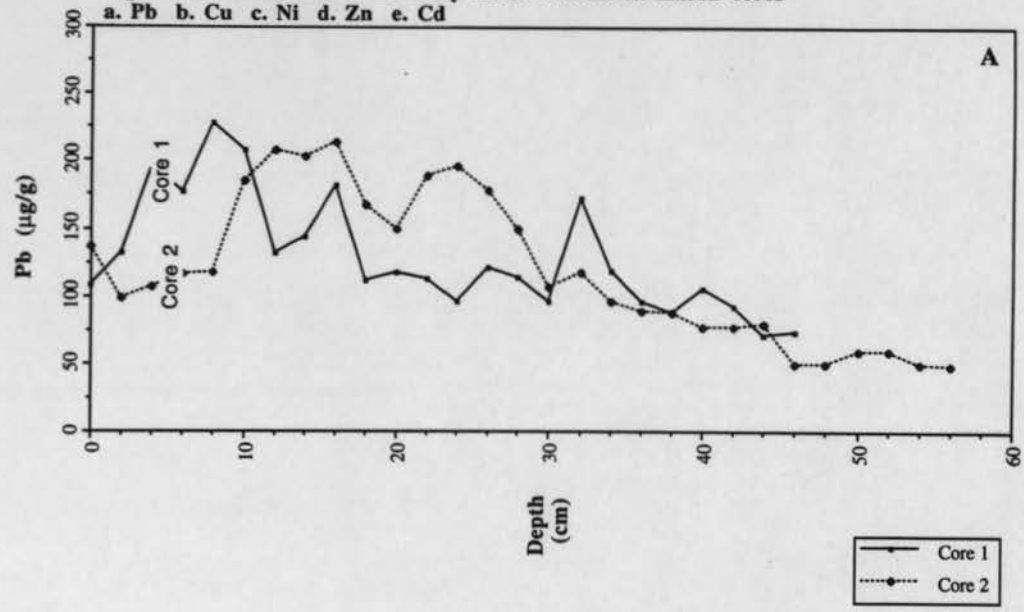
ii. Total chemical extraction for heavy metals

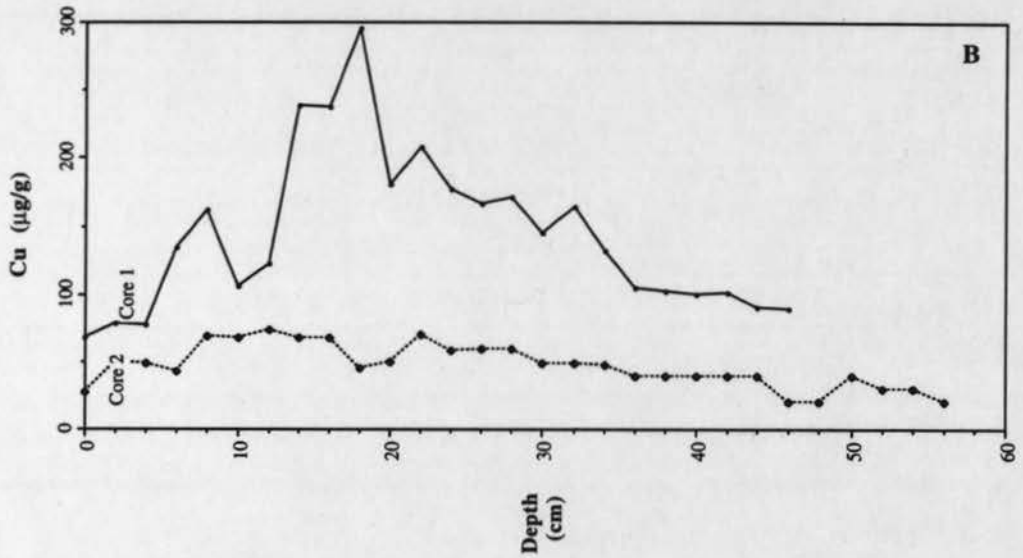
The overall trend in heavy metal concentrations is one of decreasing concentration with increasing depth. Core 2 tends to have the highest concentrations of all metals, particularly in the upper two thirds of core 1. There is a peak in all metals except Pb in core 2 at between 18 and 26 cm depth. The decline in concentration with increasing depth is smoother in core 2 with less fluctuation in value.

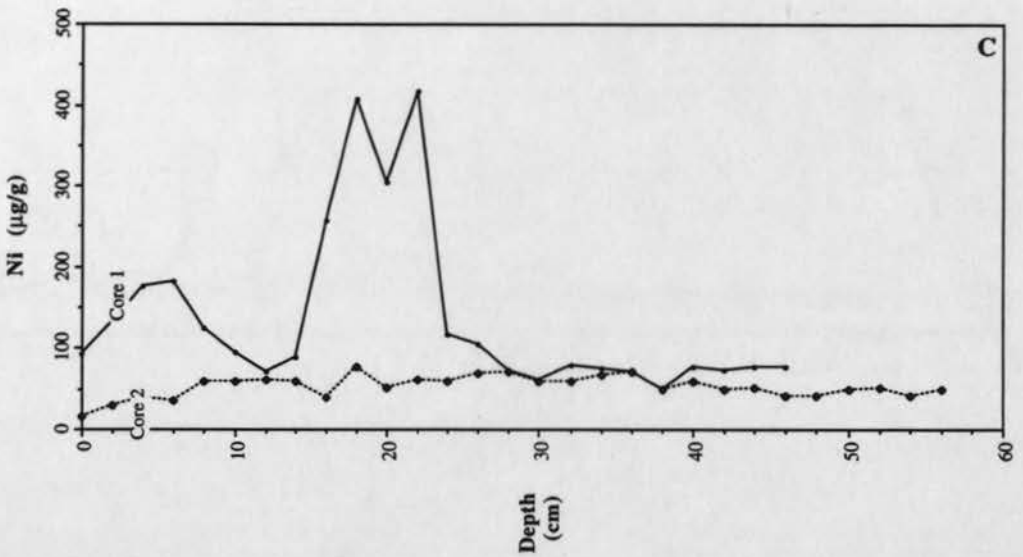
The concentration of Pb (Fig 6.7 a) fluctuates in both cores, with a peak occurring at a depth of between 10 and 22 cm in core 1 and between 6 and 14 cm in core 2. The highest concentration of 230 $\mu g\ g^{-1}$ was found in core 2 at a depth of 10 cm. Pb concentrations were higher in core 2 than core 1 in the top 12 cm, but are generally lower than core 1 below this apart from a peak at 34 cm depth when Pb concentrations reach 160 $\mu g\ g^{-1}$. The lowest value for Pb is in core 1 at 50 $\mu g\ g^{-1}$, in the basal sediments.

Cu concentrations are higher in core 2 than in core 1 (Fig 6.7 b). A peak in core 2 is found at a depth of 20 cm where the concentration of Cu reaches 300 $\mu g\ g^{-1}$. Values tend to decrease either side of this peak, declining to the lowest value of 70 $\mu g\ g^{-1}$ in the uppermost sample. Cu concentrations

Fig 6.7 Downcore trends in heavy metal content in marsh cores
a. Pb b. Cu c. Ni d. Zn e. Cd







Cd (µg/g)
0
10
20
30
40
50
60
Depth (cm)
Core 1
Core 2
E

Zn (µg/g)
0
1000
2000
3000
Depth (cm)
Core 2
Core 1
D

in core 1 do not exhibit the same pattern as found in core 2. The concentration rises from a value of 30 $\mu g\ g^{-1}$ in the top-most sample to 75 $\mu g\ g^{-1}$ at 14 cm depth and then decreases to 20 $\mu g\ g^{-1}$ in the basal samples.

Again it is in core 2 that the samples with the highest values for Ni are found (Fig 6.7 b). Two peaks in Ni concentration are found at depths of between 0 and 14 cm and 16 to 26 cm where values reach 190 and 420 $\mu g\ g^{-1}$ respectively. Ni levels in Core 1 never exceed those of core 2, but at a depth of between 38 and 40 cm they both fall to between 50 and 75 $\mu g\ g^{-1}$. The highest level in core 1 is at a depth of 20 cm with a value of 80 $\mu g\ g^{-1}$.

The highest concentration of Zn (Fig 6.7 c) is found in the peak at a depth of between 16 and 26 cm in core 2 where values reach 2800 $\mu g\ g^{-1}$. The highest level in core 1 is found at a similar depth to the peak in core 2, at a depth of 24 cm, but the concentration is significantly lower at 700 $\mu g\ g^{-1}$. Values above the peak in core 2 are lower than those below the peak at about 250 and 500 $\mu g\ g^{-1}$ respectively. Zn values in core 1 exceed those of core 2 only at between 8 and 16 cm depth where they reach 50 $\mu g\ g^{-1}$. In the top 6 cm the Zn concentration of core 1 is 250 $\mu g\ g^{-1}$, and at the base it is 200 $\mu g\ g^{-1}$.

The profile for Cd in both cores (Fig 6.7 c) is very similar to that of Zn, with a peak in concentration in core 2 at a depth of between 16 and 26 cm of up to 55 $\mu g\ g^{-1}$. There

is also a small peak at a depth of 8 cm where values reach 16 $\mu g\ g^{-1}$. Below these peaks, values drop to a minimum of 2 $\mu g\ g^{-1}$ in the basal samples. Cd concentration is below the limits of detection in the uppermost sample of core 1. It rises slowly to 8 $\mu g\ g^{-1}$ at 14 cm, dropping gradually to a value of 3 $\mu g\ g^{-1}$ at the base of the core. Cd levels in core 1 only exceed those of core 2 at between 12 and 14 cm depth and at the base of the core at depths of 42 and 46 cm, but the difference is small.

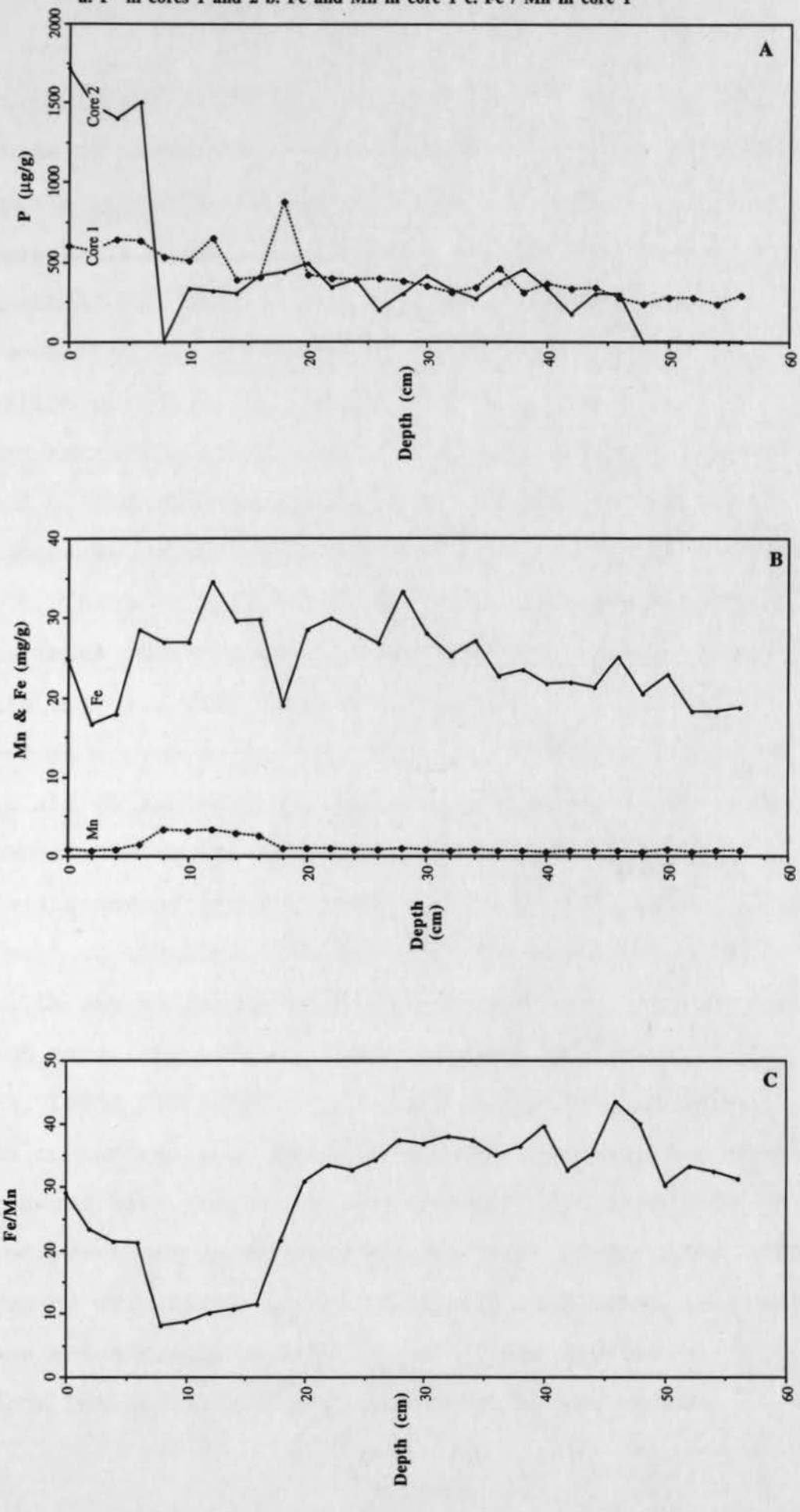
Section 6.7.2 compares maximum heavy metal concentrations and F values from the individual components of Wyken Slough to assess the relative enrichment of these deposits.

Heavy metal data from these analyses will be used in Chapter 7 to calculate metal budgets in Wyken Slough and to assess the amount of selected heavy metals stored in the sediments of the marsh. Section 6.6 will apply water quality data to consider the stability of the marsh as a sink for heavy metals.

iii. P, Fe and Mn

P analysis was carried out on both cores (Fig 6.8 a); the highest values being recorded in the upper samples of core 2 where the top sample is 1700 $\mu g\ g^{-1}$. The top sample of core 1 was 600 $\mu g\ g^{-1}$. These differences can be explained since core 2 was located along the eastern side of the marsh (Fig 2.11 a) where the highest values of P were found in the upper

Fig 6.8 Downcore trends in P, Fe, Mn and Fe / Mn in marsh cores
a. P in cores 1 and 2 b. Fe and Mn in core 1 c. Fe / Mn in core 1



sediments. This may reflect the higher productivity of the eastern side of the marsh associated with an unimproved stream rising from a predominantly agricutural catchment. Values below these are similar in both cores apart from a small peak in concentration in core 1 at 20cm depth, of 870 $\mu g\ g^{-1}$. Lowest concentrations are found in the basal samples at a concentration of 300 $\mu g\ g^{-1}$ for both cores.

Fe and Mn analysis was carried out on core 1 and is shown in Fig 6.8 b. The highest values were recorded in the upper samples where Fe values reach almost 35 $mg\ g^{-1}$ and Mn reaches 3.5 $mg\ g^{-1}$. There is a distinct region of the core between 3 and 10 cm depth where values increase in both Fe and Mn before they again decrease with increasing depth.

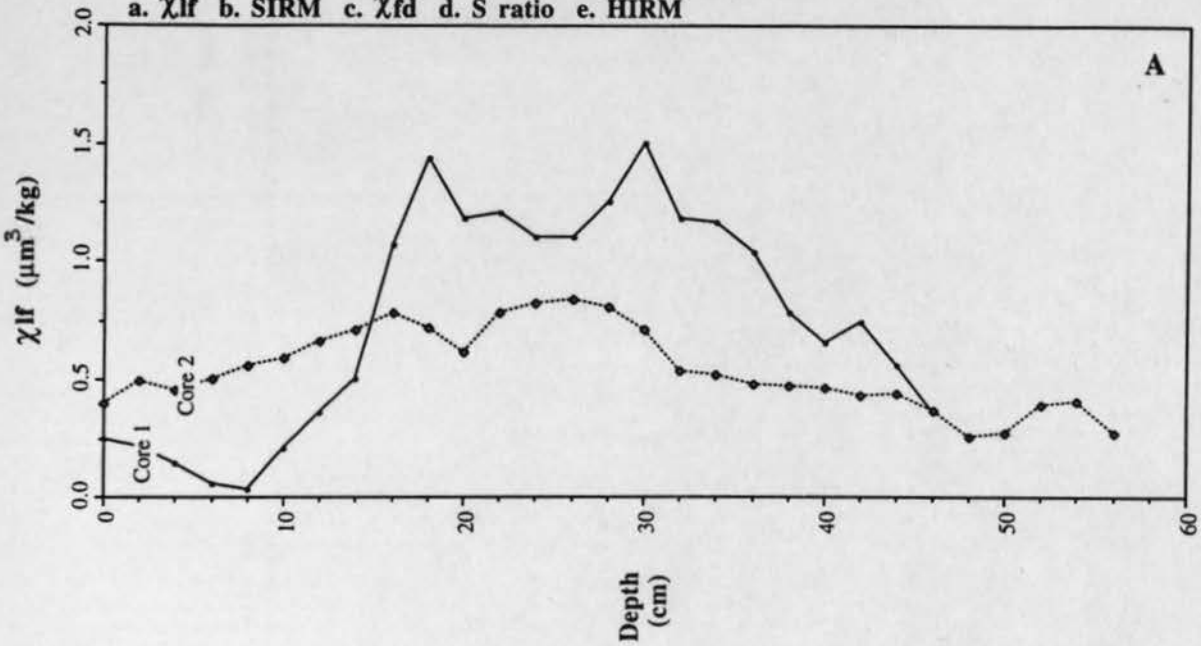
Fe and Mn appear to show a change in redox conditions at between 6 and 20 cm depth in the core. The upper 4 cm appears to be reduced due to the anaerobic bacteria found in the surface sediments of wetland sediments (Williams, 1990). It is in this part of the core that increased P levels are also found, which may be linked to bacterial activity. In the marsh plant root zone, the sediments are oxidised (Mitsch & Gosselink, 1993) reflected in slightly higher Fe and much higher Mn concentrations. Beneath the rooting zone, sediments become reduced with increasing depth due to the anaerobic conditions prevalent in waterlogged sediment. Plants are able to survive by structural adaptations to living under anaerobic conditions and aerenchyma (air spaces) allow diffusion of oxygen from the aerial parts of the plant to the roots.

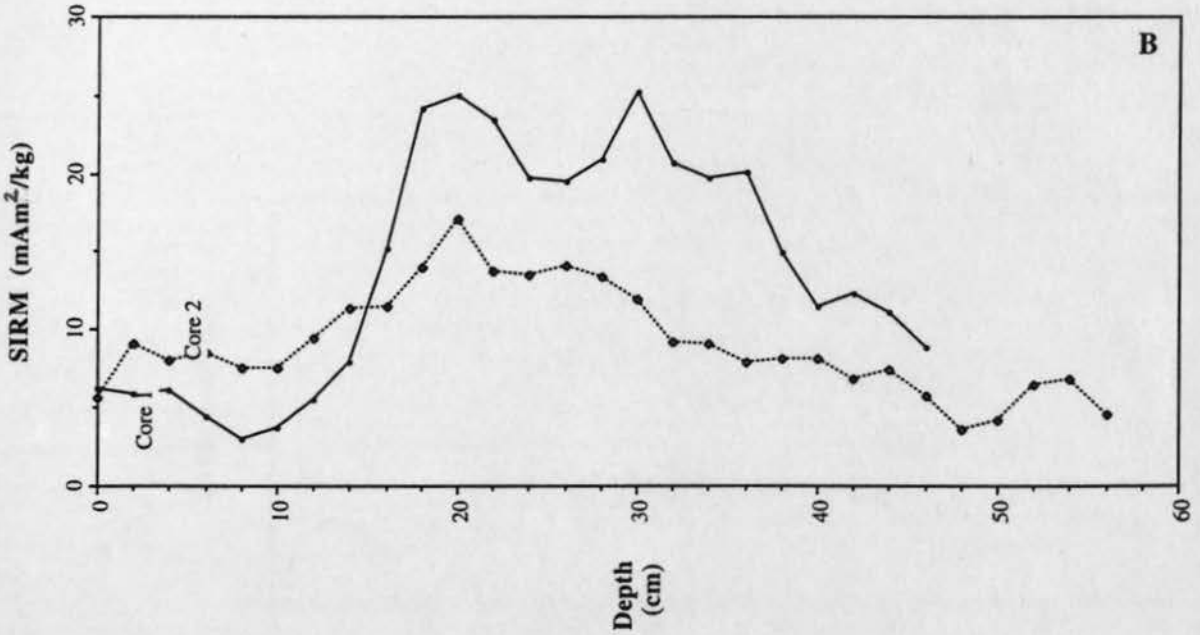
Beneath the rooting zone, the rate of diffusion of oxygen can be up to 10,000 times slower than that in a normally well-aerated soil (Gambrell & Patrick, 1978), hence the conditions are reducing.

iv. Mineral magnetic measurements.

χ_{lf} and SIRM data for both cores are plotted in Fig 6.9 a and b. Trends for χ_{lf} and SIRM are similar for both cores which exhibit an increase below a depth of 10 cm with peaks at between 20 and 32 cm. Values subsequently decline towards the base of the cores. The highest values of both magnetic parameters are found in core 1 where SIRM reaches 25 $mAm^2\ kg^{-1}$ and χ_{lf} reaches 1.5 $\mu m^3\ kg^{-1}$. The highest values for core 2 are 0.8 $\mu m^3\ kg^{-1}$ and 17.5 $mAm^2\ kg^{-1}$ for χ_{lf} and SIRM respectively. The lowest values for both cores are in the uppermost samples, those for core 1 being the lowest with SIRM values of 3 $mAm^2\ kg^{-1}$ and χ_{lf} of less than 0.1 $\mu m^3\ kg^{-1}$. In core 2 the lowest values are 0.4 $\mu m^3\ kg^{-1}$ for χ_{lf} and 6 $mAm^2\ kg^{-1}$ for SIRM. χ_{fd}, S-ratio and HIRM for both marsh cores are presented in Fig 6.9 c - e. χ_{fd} values are low, particularly in core 1 from the uppermost sample down to 8 cm where there was no recordable difference. Core 2 has slightly higher values of χ_{fd}, with an average of about 0.2 $nm^2\ kg^{-1}$ and a peak to over 0.5 $nm^3\ kg^{-1}$ at a depth of 10 cm. The S-ratio is slightly higher in core 2 than core 1 with values approaching

Fig 6.9 Mineral magnetic characteristics of marsh cores 1 and 2
a. χlf b. SIRM c. χfd d. S ratio e. HIRM



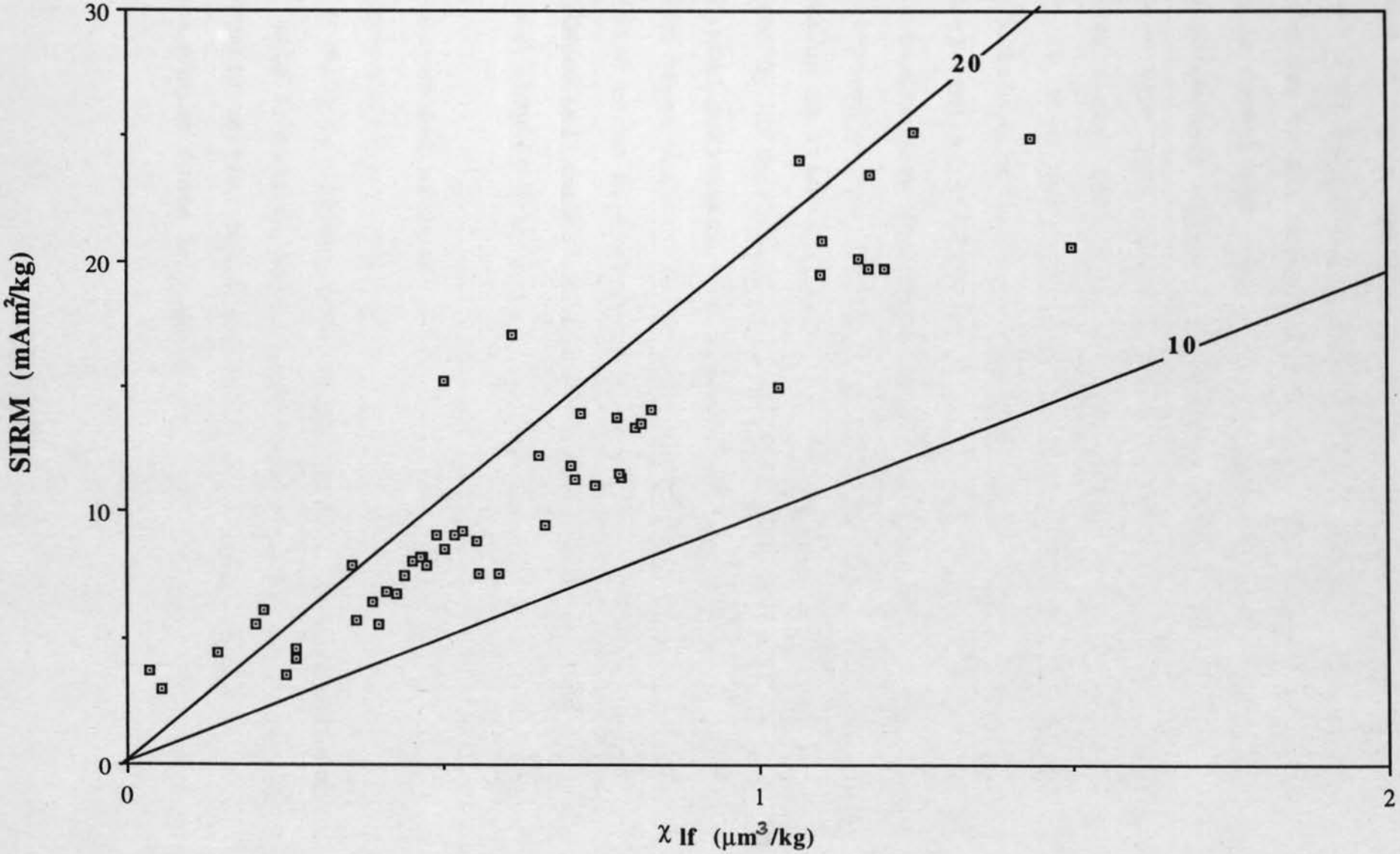


HIRM (mAm²/kg)
0
1
2
3
4
5
Core 1
Core 2
Depth (cm)
0
10
20
30
40
50
60
E

S ratio
0.5
0.6
0.7
0.8
0.9
1.0
1.1
Core 1
Core 2
Depth (cm)
0
10
20
30
40
50
60
D

χfd (nm³/kg)
0
10
20
30
40
50
60
Core 1
Core 2
Depth (cm)
0
10
20
30
40
50
60
C

Fig 6.9 f Scattergram of χlf against SIRM for both marsh cores



1 at 5 cm depth. There is a decrease in value at 11 cm followed by relatively constant values of ca. 0.75 which are maintained to the bottom of the core. The S-ratio fluctuates less in core 1 and remains at a fairly steady average value of 0.75 throughout the core. HIRM varies widely in core 1, ranging from just over 0.5 $mAm^2\ kg^{-1}$ in the uppermost samples to over 4 $mAm^2\ kg^{-1}$ at 11 cm depth. Core 2 is variable in the upper 12 cm of the core, ranging from 0 to more than 4 $mAm^2\ kg^{-1}$ within 6 cm. Below the peak at 11 cm, the trend is for a gradual decline in values.

A scattergram of SIRM with χ_{lf} is presented in Fig 6.9 f. Superimposed on the scattergram are gradients which represent ratios of 10:1 and 20:1, lines which delineate the area covered by MD ferrimagnetic particles such as particulate associated pollutants. The majority of the samples fall between these ratios, so the marsh sediment appears to be dominated by MD ferrimagnetic grains such as particulate associated pollutants (Thompson & Oldfield, 1986. See also Fig 4.16 and Chapter 2.10 ie).

6.3. Stream bed samples

This section is divided into three parts which consider total heavy metals, mineral magnetic measurements and P, Fe and Mn and organic matter. Descriptions of the sediments from the streams can be found in Appendix 3.

i. Total chemical extract for heavy metals

Since the reason for obtaining stream bed samples was to assess the potential store of heavy metals in these materials, rather than an exhaustive assessment of the spatial distribution of the elements in the fluvial system, the results are presented as groups of data based on river reaches. These groupings are illustrated schematically in Fig 2.11 c. The single sample taken from Bayton Road at site 2 (Fig 2.11 b for location) was found to be exceptionally high in Cu, Ni and Zn and therefore two averages were calculated for these samples one including BR2, given in parenthesis, and one without this sample.

To put the heavy metals concentrations from the Wyken Slough streams in context, background values were necessary for comparison. The agricultural reaches were used for compar tive purposes since they were site-specific and were not subjected to the amount of contamination by industry and from the atmosphere as the rest of the streams draining Wyken Slough. However, it is likely that they are in receipt of a certain amount of contaminants from the atmosphere. To test their suitability as measures of background value, they were compared with published background values from fossil river sediments and values obtained from isolated sites quoted from the Wolfson Geochemical Atlas (WGA) (1978). These values are shown in Table 6.1.

Table 6.1 Background concentrations of heavy metals from fossil river sediments and the Wolfson Geochemical Atlas (1978), compared average concentrations from the inflowing streams of Wyken Slough ($\mu g\ g^{-1}$).

	1	2	3
Zn	105	0-200	150.5
Ni	51	0 -40	47.2
Cu	25	0 -30	5.1
Pb	16	0 -80	103.8
Cd	0.2	0 - 1	2.2

1. Fossil river bed sediments (Förstner & Salomons, 1981)
2. Wolfson Geochemical Atlas (1978)
3. Average agricultural reaches at Wyken Slough

In comparison with fossil and WGA river bed sediment concentrations of heavy metals, the values for the agricultural reaches all appear to lie within background levels except for Pb which is slightly higher and Cd which is up to ten times published values. The higher concentrations for Pb and Cd were also found in the background values used to calculate enrichment factors for the lake sediments (Chapters 4.2.4 and 5.2.4), and seems to be further evidence for these values reflecting local geology rather than cultural enrichment effects. Background values for comparative purposes

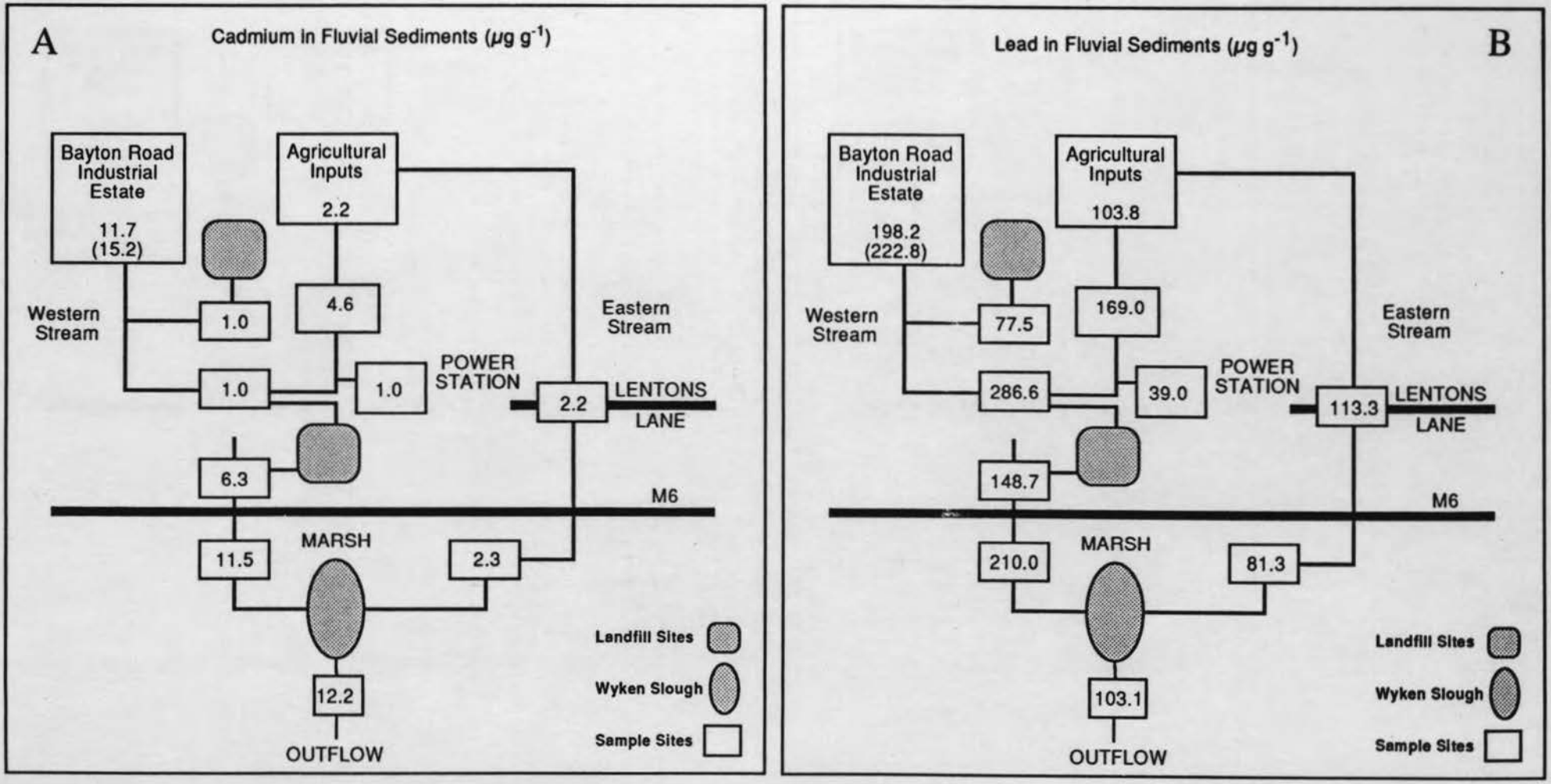
were therefore taken from the rural reaches of the northern part of the catchment.

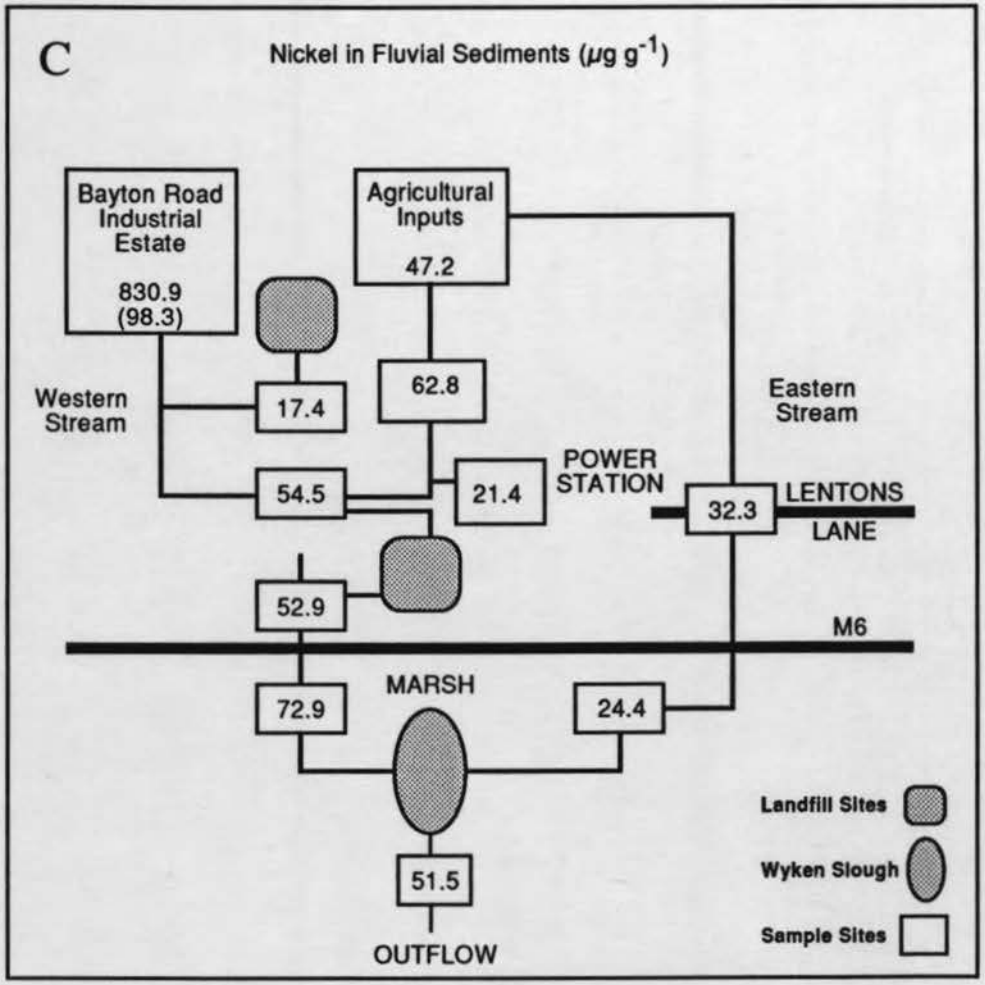
Cd data (Fig 6.10 a) indicate a low background in rural sediments with an average of 2.2 $\mu g\ g^{-1}$ coming into the lake from the eastern stream. Highest levels derive from the Bayton Road Industrial Estate with concentrations of 11.7 $\mu g\ g^{-1}$ (including sample BR2) or 15.2 $\mu g\ g^{-1}$ (excluding sample BR2). These sediments undoubtedly influence concentrations downstream where they reach 11.5 $\mu g\ g^{-1}$ in the stream sediment immediately upstream of the lake. There is little evidence of high Cd concentrations in the toxic tip leachates although higher than background values of 6.3 $\mu g\ g^{-1}$ are recorded in the reach of the main river upstream of the power station. In comparison with the rest of the fluvial system, the concentration of Cd for the outlet sediments is fairly high at 12.2 $\mu g\ g^{-1}$.

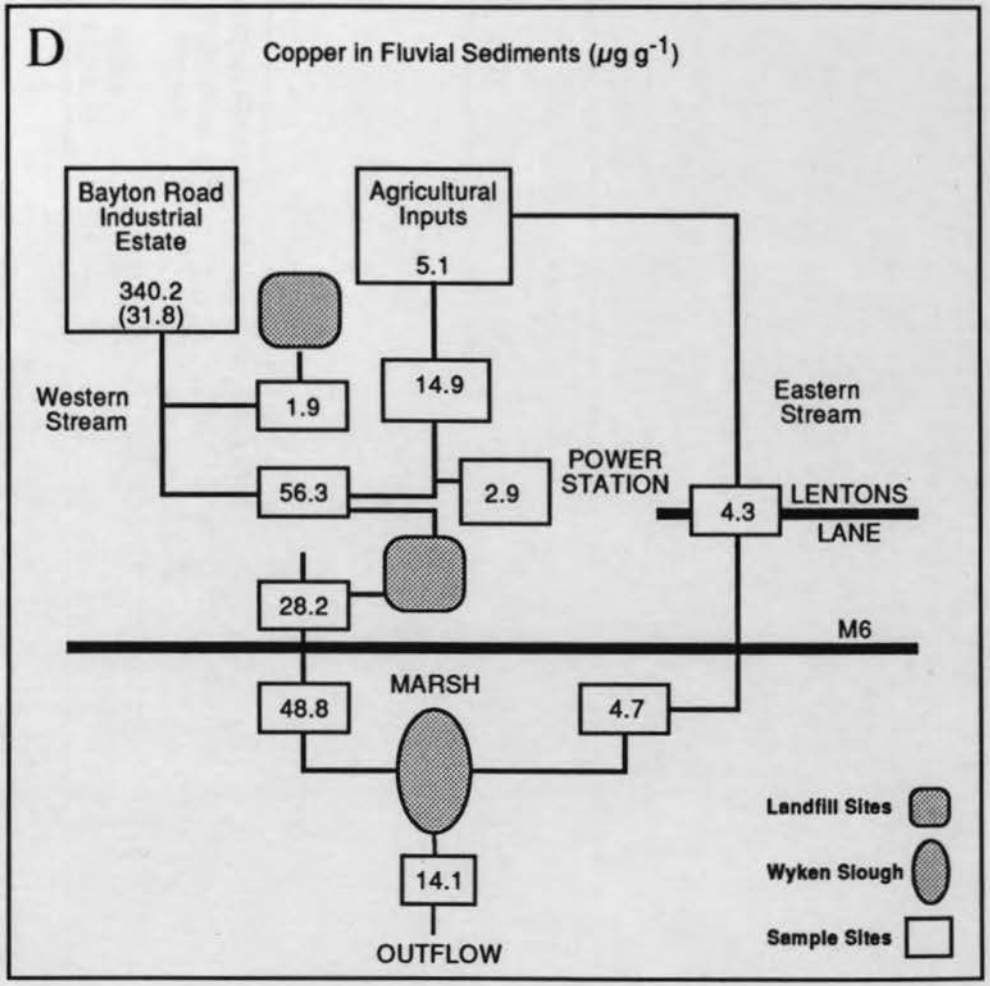
Pb data (Fig 6.10 b) show similar trends, although background levels in the rural parts of the catchment are also high at over 100 $\mu g\ g^{-1}$. As with Cd, there is little evidence for significantly elevated levels of Pb in the streams leading from the toxic tip or from the eastern stream with levels of 210.0 and 81.3 $\mu g\ g^{-1}$ respectively. The concentration of Pb in fluvial sediments downstream from the Wyken Pool outlet lies between the average values found in the eastern and western streams at 103.1 $\mu g\ g^{-1}$.

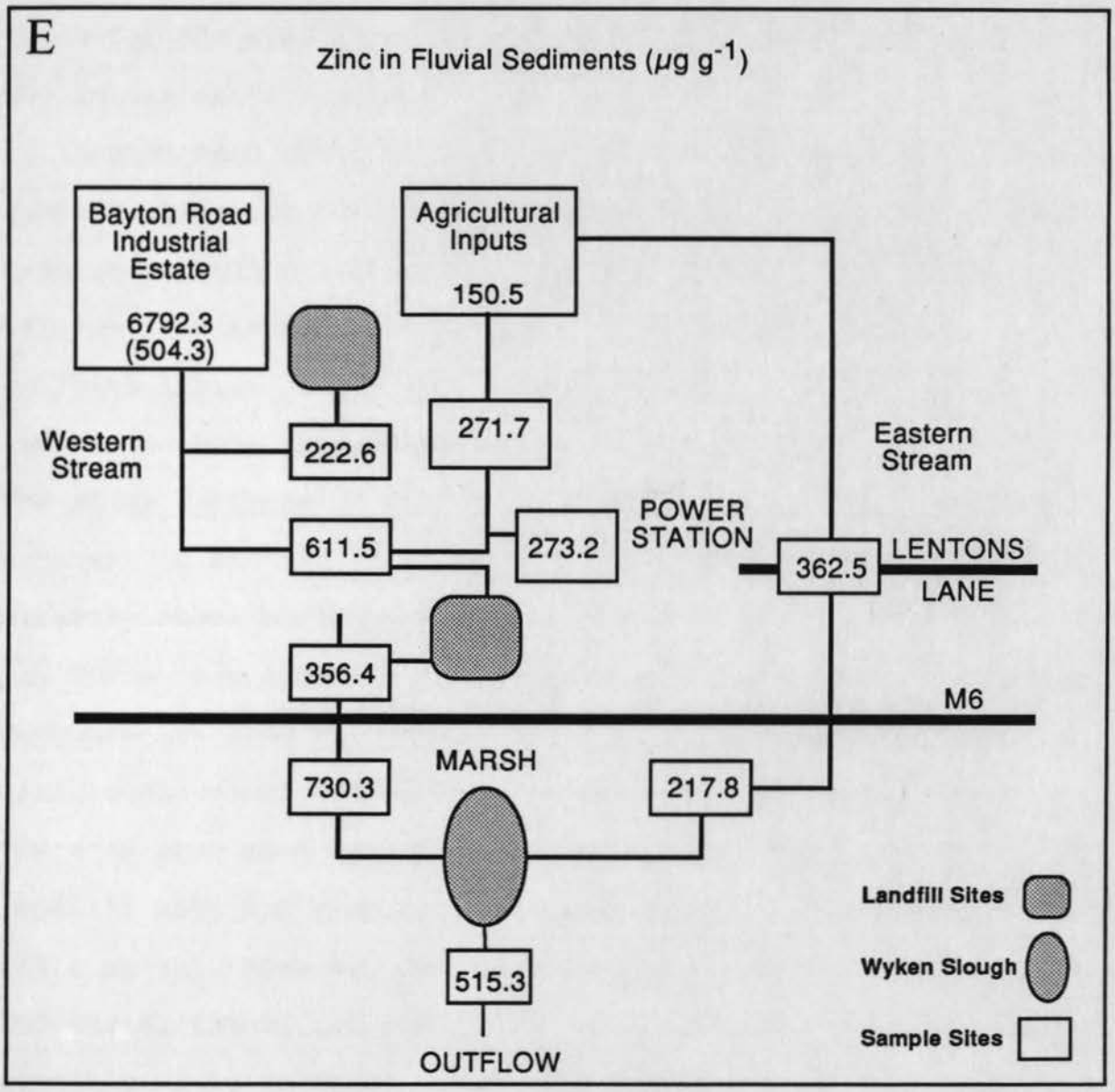
The trends in Ni data (Fig 6.10 c) are similar to those of Cd and Pb. Background concentrations in the northern reaches are below 50 $\mu g\ g^{-1}$, whereas average concentrations from the Bayton Road, including that of sample BR2, exceed 800 $\mu g\ g^{-1}$.

Fig 6.10 Schematic diagram of the distribution of heavy metals in stream bed sediments
a. Cd
b. Pb
c. Ni
d. Cu
e. Zn




C
Nickel in Fluvial Sediments (μg g-1)
Bayton Road Industrial Estate
830.9
(98.3)
Agricultural Inputs
47.2
Western Stream
17.4
62.8
Eastern Stream
54.5
21.4
POWER STATION
32.3
LENTONS LANE
52.9
M6
72.9
MARSH
24.4
51.5
OUTFLOW
Landfill Sites
Wyken Slough
Sample Sites


D
Copper in Fluvial Sediments (μg g-1)
Bayton Road Industrial Estate
340.2
(31.8)
Agricultural Inputs
5.1
Western Stream
1.9
14.9
Eastern Stream
56.3
2.9
POWER STATION
4.3
LENTONS LANE
28.2
M6
48.8
MARSH
4.7
14.1
OUTFLOW
Landfill Sites
Wyken Slough
Sample Sites


E
Zinc in Fluvial Sediments (μg g-1)
Bayton Road Industrial Estate
6792.3
(504.3)
Agricultural Inputs
150.5
Western Stream
222.6
271.7
Eastern Stream
611.5
273.2
POWER STATION
362.5
LENTONS LANE
356.4
M6
730.3
MARSH
217.8
515.3
OUTFLOW
Landfill Sites
Wyken Slough
Sample Sites

However, values without sample BR2 only approach 100 $\mu g\ g^{-1}$, so the Bayton Road Industrial Estate appears to be the major source of Ni in the catchment. This high value is reflected in generally higher concentrations in the western inlet of 72.9 $\mu g\ g^{-1}$ compared with the eastern stream just above the lake at 24.4 $\mu g\ g^{-1}$. Once again, there are no significantly high values found in sediments downstream of the landfill. The value for the sediments in the outlet are between those from the inlets at 51.5 $\mu g\ g^{-1}$.

Bayton Road provides the samples with the highest concentrations of Cu (Fig 6.10 d). The value obtained for the samples including BR2 is 340.2 $\mu g\ g^{-1}$, whereas the average without this sample is 31.8 $\mu g\ g^{-1}$. The eastern stream exhibits little Cu enrichment, averaging 4.3 $\mu g\ g^{-1}$. Small increases above background are to be found in the reaches of the river upstream of the power station (14.9 $\mu g\ g^{-1}$) and adjacent to the tip (56.3 $\mu g\ g^{-1}$). The value for the outlet is slightly above background at 14.1 $\mu g\ g^{-1}$.

There is evidence for significantly higher than background Zn concentrations in the streams around Hawksbury landfill, with levels varying from 222.6 to 611.5 $\mu g\ g^{-1}$ (Fig 6.10e). There is also some contamination centred on the lorry park and landfill site upstream of Lentons Lane, where values reach 362.5 $\mu g\ g^{-1}$. However, Zn concentrations from the Bayton Road Industrial Estate (excluding BR2) are more than 3 times, and possibly up to 45 times (including sample BR2) higher than background concentrations recorded in samples located in the north of the catchment. The concentration of Zn in the outlet

sample lies between the values of the two inflowing streams at 515.3 $\mu g\ g^{-1}$.

Bayton Road Industrial Estate consistently provided the sample with the highest heavy metal concentration, particularly Cu, Ni and Zn although values for Cd and Pb are fairly high also.

Table 6.2 compares maximum values of heavy metals from Wyken Slough stream bed samples with other studies of rivers from areas subjected to various activities (Thoms, 1987). These show that the stream bed sediments are particularly enriched with respect to Zn and Ni, but that rivers located in areas of mining have concentrations of some heavy metals which are up to forty times that of the Wyken Slough streams.

Section 6.7.2 summarises the heavy metal concentrations from Wyken Slough and compares the maximum concentrations and F values from each component. The following section considers concentrations and F values at the individual reach scale.

In order to estimate the relative increase in heavy metals, cultural enrichment values (F) were calculated. The maximum values of heavy metal concentrations from the stream bed sediments are presented in Table 6.3 and are based on the groupings shown in Fig 2.11 c.

Table 6.2 Maximum published heavy metal concentrations of bed sediments from rivers subjected to various activities within their catchments compared with concentrations obtained from Wyken Slough Brook ($\mu g\ g^{-1}$).

	1	2	3	4	5
Cd	15	54	43	13	30
Cu	340	2001	5050	500	2600
Ni	800	1020	949	310	416
Pb	210	575	8000	1430	2100
Zn	7000	6114	7000	6220	2500

1. Wyken Slough Brook
2. River Thame
3. River in mining area
4. River in industrialised area
5. River in urbanised area

2 - 5 above from Thoms (1987)

Table 6.3 Average heavy metal concentrations from the Wyken Slough streams ($\mu g\ g^{-1}$).

	1	2	3	4	5
Zn	150.5	362.5	730.3	6792.3	515.3
Ni	47.2	32.3	98.3	830.9	51.5
Cu	5.1	4.7	56.3	340.2	14.1
Pb	103.8	113.3	286.6	198.2	103.1
Cd	2.2	2.3	15.2	11.7	12.2

1. Average agricultural reaches at Wyken Slough used as background
2. Eastern stream below the agricultural reaches
3. Western stream below the agricultural reaches without sample BR2
4. Average Bayton Road samples including sample BR2
5. Outflow

Heavy metal concentrations from the agricultural reaches (given in Table 6.3) were used as background in the calculation of F values, the method for which is given in Chapter 4.2.4. The F values for the stream sediments are given in Table 6.4.

Table 6.4 Enrichment factors (F) for selected reaches of the streams flowing through Wyken Slough.

	1	2	3	4
Zn	2.4	4.9	45.1	3.4
Ni	0.68	2.1	17.6	1.1
Cu	0.92	11.04	66.7	2.8
Pb	1.1	2.8	1.9	0.99
Cd	1.05	6.9	5.3	5.6

1. Eastern stream
2. Western stream without sample BR2
3. Bayton Road including sample BR2
4. Outlet

These values show that, with the exception of Zn, the eastern stream is not enriched in heavy metals in comparison with background. The excess Zn found in the sediments of the eastern stream may represent atmospheric deposition from local industry, runoff from the M6 motorway, or may be associated with the lorry park north of Lentons Lane (Fig 2.11 b). The western stream as a whole is enriched in all heavy metals, in particular Cu but also Cd and Zn. Comparison of the western stream with just Bayton Road shows that the Industrial Estate may influence the enrichment of Cu and Zn since these are particuarly high here. The outlet is enriched in Zn, Cu and

Cd, reflecting the upstream sources of these metals from the western stream. However, values of F are very much lower than those obtained for the western stream, and suggests that the lake may be acting as a settling tank for some of the heavy metals before they reach the outlet.

Analysis of the bed sediments from the inflowing streams and from the outlet at Wyken Slough highlight the importance of the Industrial Estate as a source of heavy metals. The Estate was built in the 1960s (Chapter 3.4.2) and so will have been contributing excess metals to the system for the last 30 years via the western stream. For the first 10 - 15 years of the operating life of the Industrial Estate, the marsh was intact, but in the late 1970s (Chapter 3.4.2) drainage was improved by the cutting of a drainage ditch through the western side of the marsh. This would have resulted in any contaminated sediments having an umimpeded passage through the fluvial system and into the lake. Many of the polluting industries on the Estate such as the Ni-Cd battery factory and the Zn plating works are now no longer in operation (J. Batty, NRA (Severn Trent Region), pers comm) or have taken steps to reduce the contamination potential of their effluent. Even so, this study has shown that heavy metals are stored in the fluvial bed sediments and may still pose a threat to the environment should conditions change. Section 6.6 examines the water quality of the stream and lake water and compares this with results of heavy metals analysis of both marsh and stream bed sediments in terms of the capacity of prevailing conditions within the catchment to remobilise metals at present stable in sediment sinks.

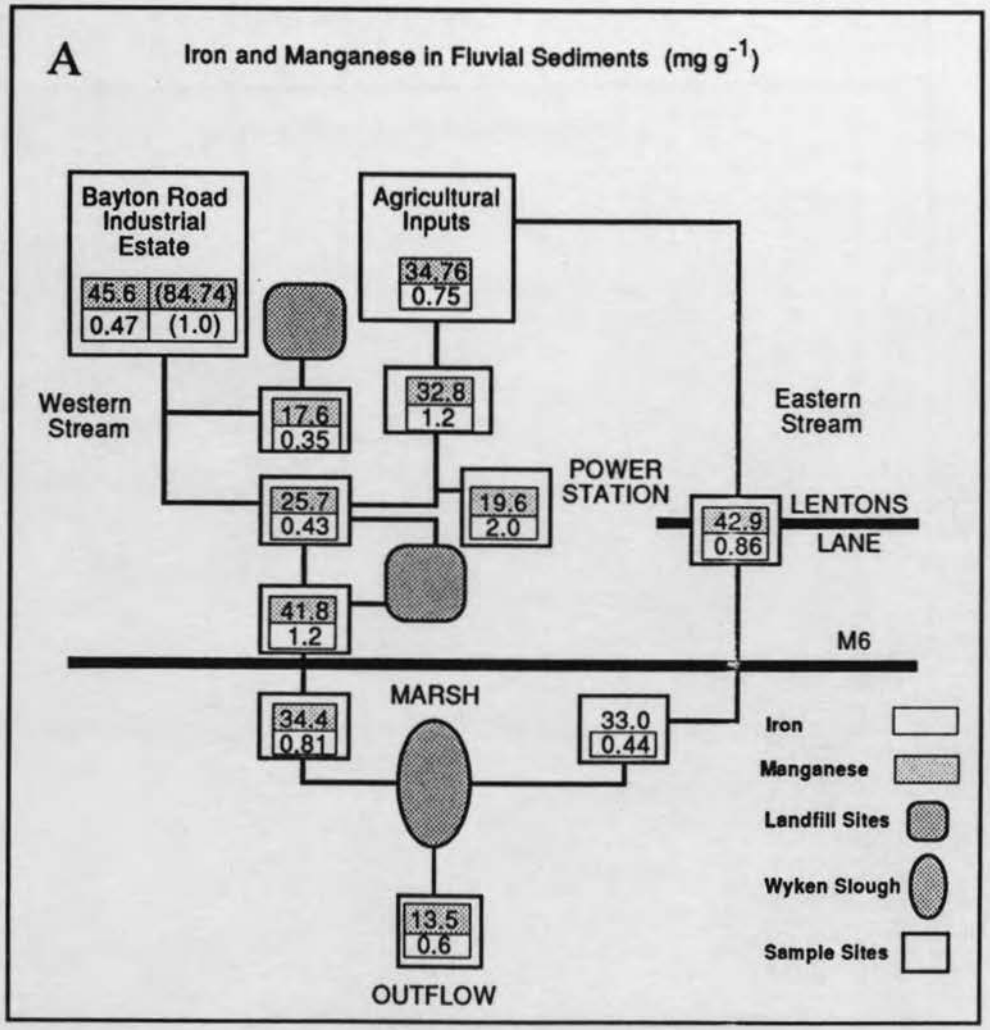
ii. Fe and Mn, organic matter and P

Fe concentrations (Fig 6.11 a) range from 45.56 mg g^{-1} in the Bayton Road sediments, including sample BR2, and 42.9 mg g^{-1} in the reach passing under Lentons Lane to the samples downstream of the landfill sites which range from 32.8 to 17.6 mg g^{-1}. The higher concentrations for Mn were found in the area downstream of the power station (1.95 mg g^{-1}), with lower values found in the river reach passing through the marsh into the lake on the eastern side (0.44 mg g^{-1}) and downstream of the landfill sites (0.35 mg g^{-1}). The Fe/Mn ratio is presented on Fig 6.11b and shows the highest ratios associated with the eastern stream, particularly before it passes through the marsh (75.0) and with the reaches associated with Lentons Lane (50). The lowest ratios are found in reaches adjacent to the Bayton Road Industrial site (7.7) and the power station (10.1).

Organic matter (Fig 6.12 a) in the fluvial sediments ranges from 5.5% to 23.9%. The highest percentages are found in the sediments downstream of Bayton Road Industrial Estate and also (18.9%) near the power station and (16.3%) upstream of the lake in the western inlet bed sediments. These values are similar to those of the lake sediments (Fig 5.7) which average about 15%. The lowest value of 5.5% was found in the sediments downstream of the Hawksbury landfill site and (9.8%) in the sediments of the eastern stream as it passed through the marsh.

P concentrations, however, (Fig 6.12 b) are significantly lower in fluvial sediments than lake sediments; ranging from

Fig 6.11 Schematic diagram of the distribution of Fe, Mn and Fe / Mn in stream bed sediments
a. Fe and Mn
b. Fe / Mn



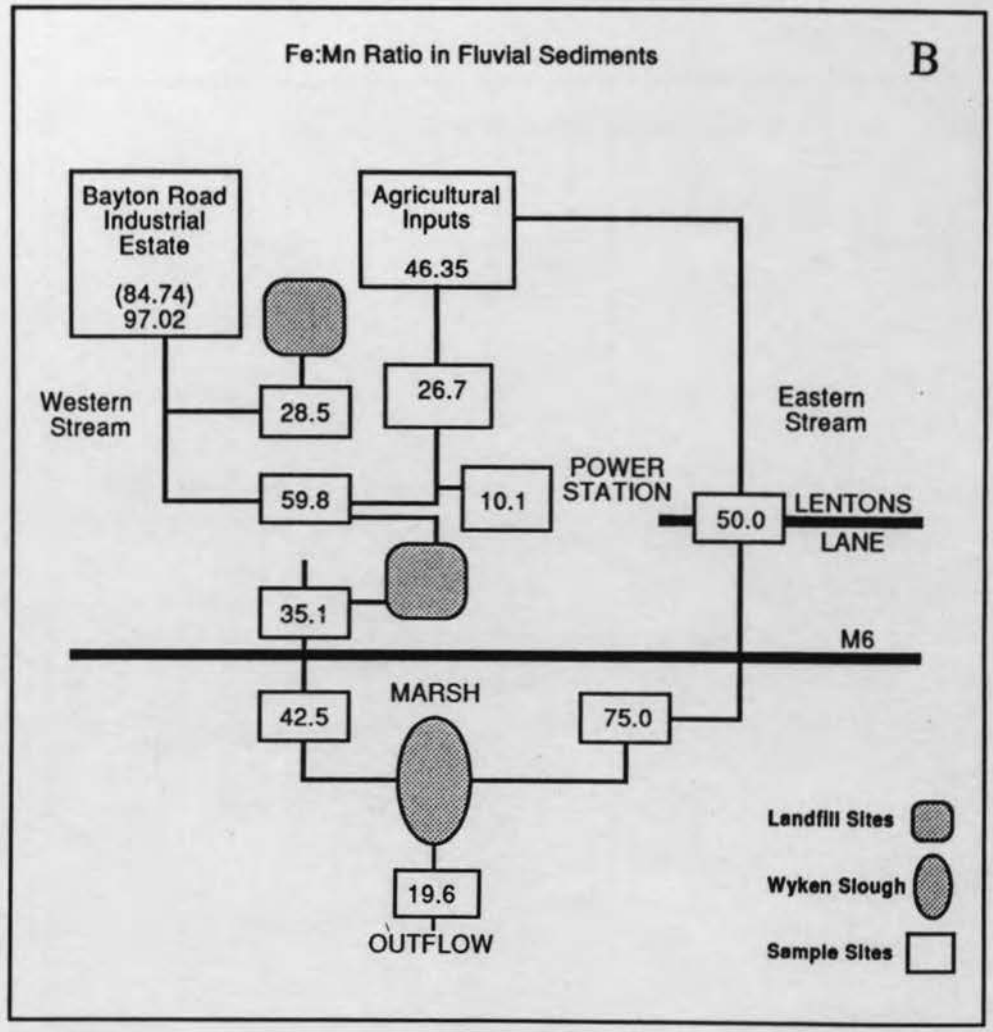
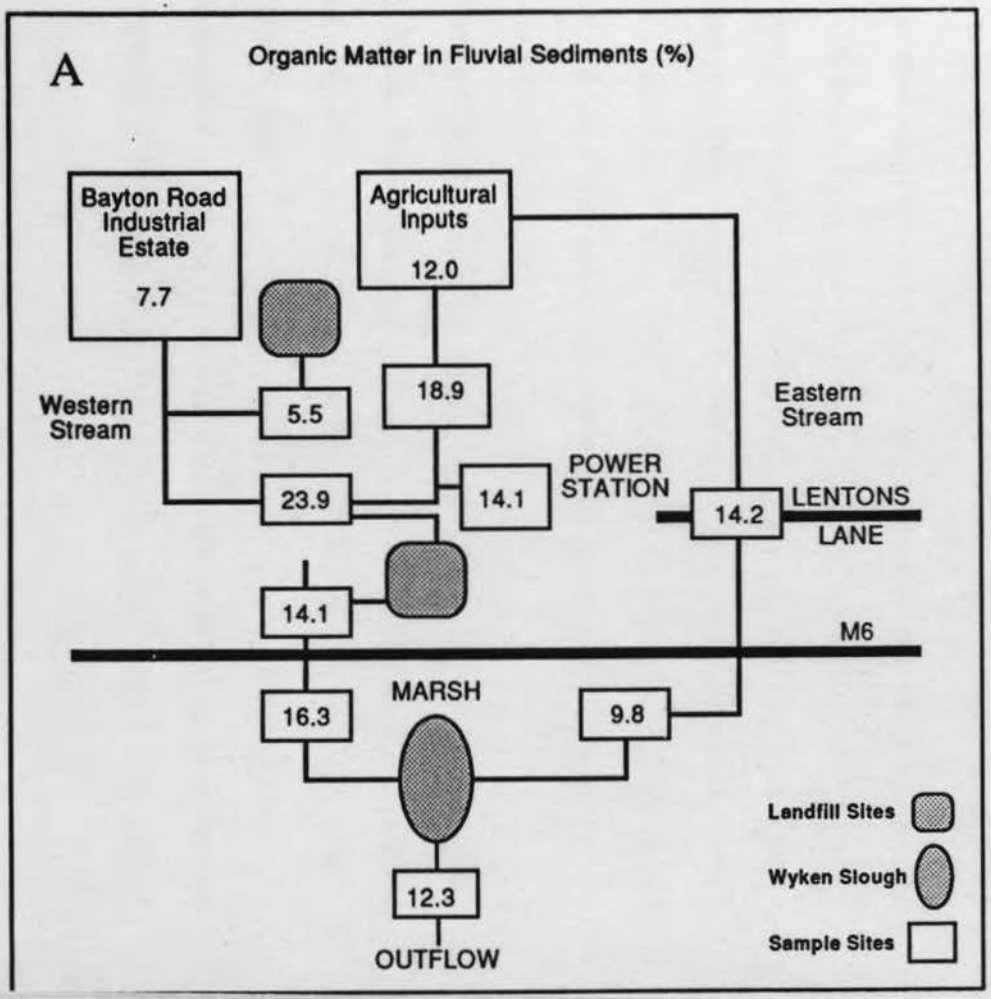
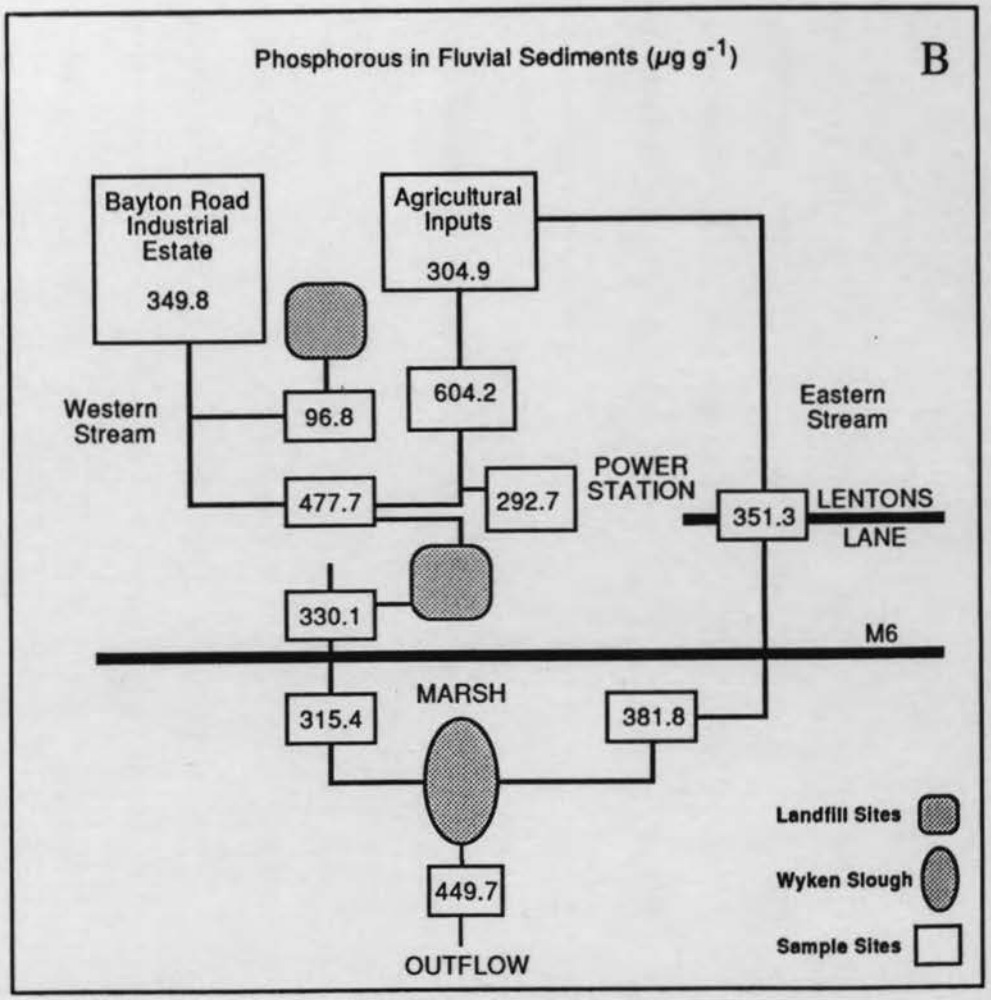


Fig 6.12 Schematic diagram of the distribution of P and organic matter in stream bed sediments
a. Organic matter
b. P





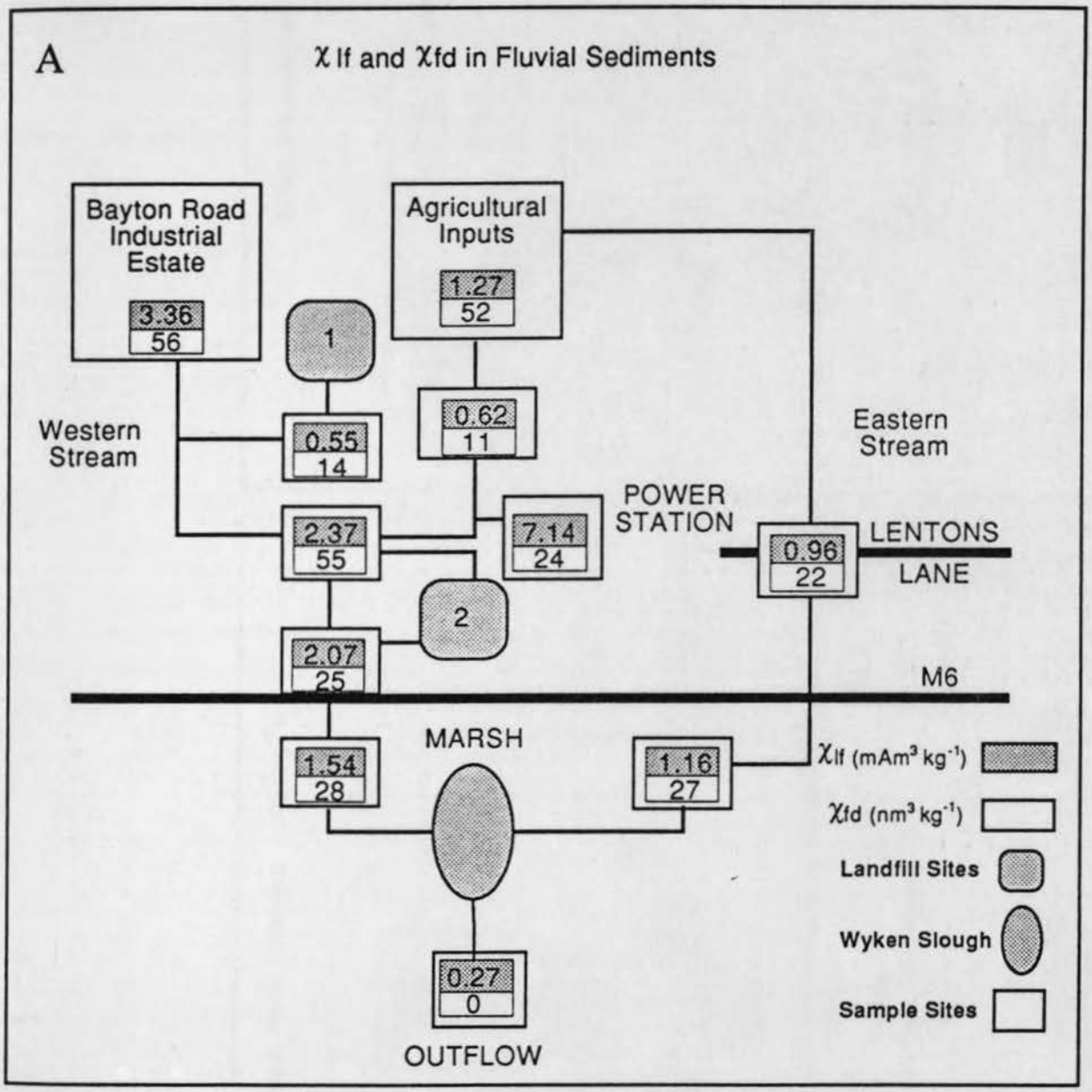
96.8 to 604.2 $\mu g\ g^{-1}$ (Fig 5.11). The higher and lower values are associated with the areas in the catchment of high and low organic matter content. Higher values were recorded for streams draining agricultural rather than industrialised areas of the basin.

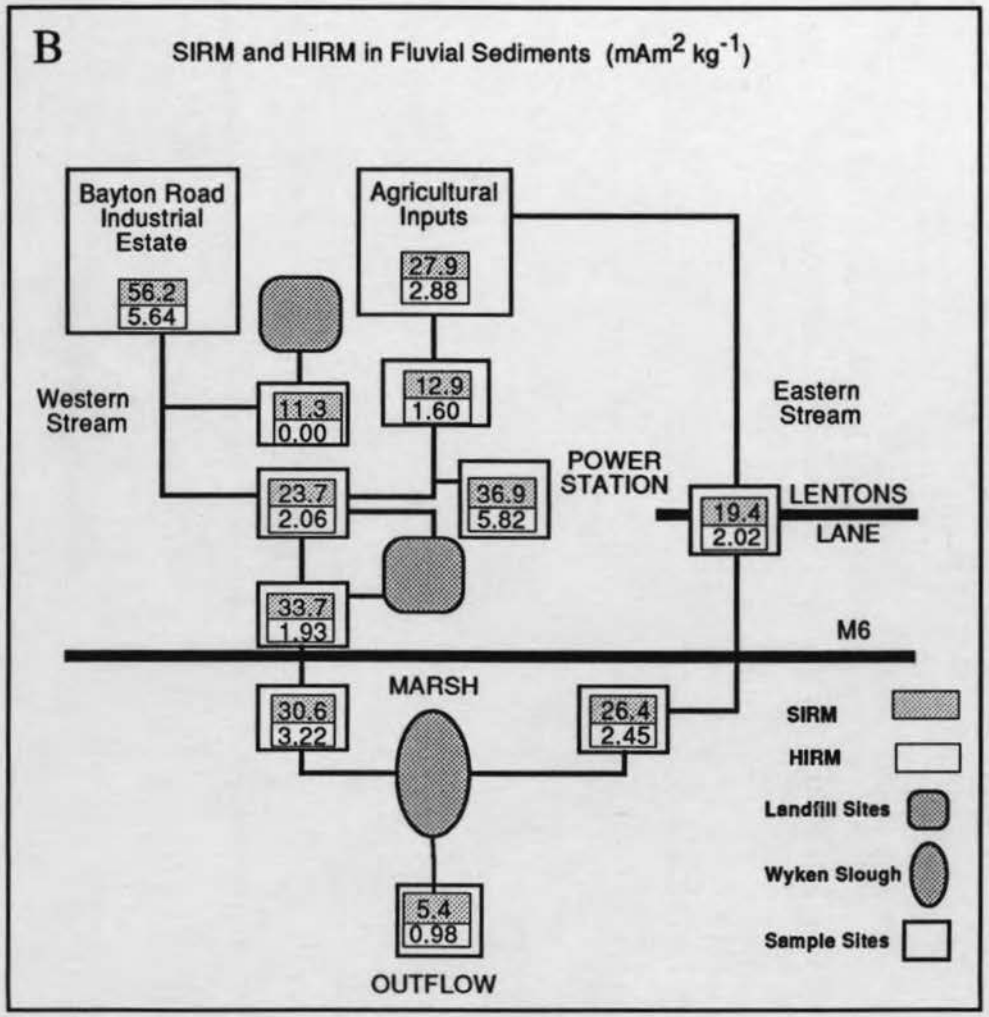
iii. Mineral magnetic measurements

Figs 6.13 a - d illustrate the mineral magnetic data for the stream samples. The highest χ_{lf} values (Fig 6.13 a) are found in the samples located around the Bayton Road Industrial Estate, reaching 3.4 $\mu m^3\ kg^{-1}$. The lowest values are associated with the outflow where the χ_{lf} is 0.27 $\mu m^3\ kg^{-1}$. χ_{fd} values are low (Fig 6.13 b) and range from 11 to 56 $nm^3\ kg^{-1}$. SIRM is shown in Fig 6.13 c, the highest values are found associated with the Bayton Road Industrial Estate at 56.18 $mAm^2\ kg^{-1}$, and lowest at the outlet at 5.38 $mAm^2\ kg^{-1}$. The S-ratio and HIRM are presented in Figs 6.13d and give an indication of the ferrimagnetic and antiferromagnetic grains in the bed sediment. The highest S-ratios are associated with both the landfill sites where values approach 1. The lowest S-ratios are found in the eastern stream and the outflow, although values are generally above 0.5.

A scattergram of SIRM versus χ_{lf} is presented in Fig 6.14. Superimposed on this scattergram are lines of gradient which represent ratios of 10:1, 20:1 and 40:1. The majority of the samples lie between the 10 and 20 ratios and are therefore dominated by MD ferrimagnetic grains such as particulate bound pollutants (Thompson & Oldfield, 1986; see also Fig 4.16 and

Fig 6.13 Schematic diagram of the distribution of mineral magnetic characteristics in stream bed sediments
a. χ_{lf} and χ_{fd}
b. SIRM
c. HIRM and S-ratio




B
SIRM and HIRM in Fluvial Sediments (mAm2 kg-1)
Bayton Road Industrial Estate
56.2
5.64
Agricultural Inputs
27.9
2.88
Western Stream
11.3
0.00
12.9
1.60
Eastern Stream
POWER STATION
23.7
2.06
36.9
5.82
19.4
2.02
LENTONS LANE
33.7
1.93
M6
MARSH
30.6
3.22
26.4
2.45
5.4
0.98
OUTFLOW
SIRM
HIRM
Landfill Sites
Wyken Slough
Sample Sites

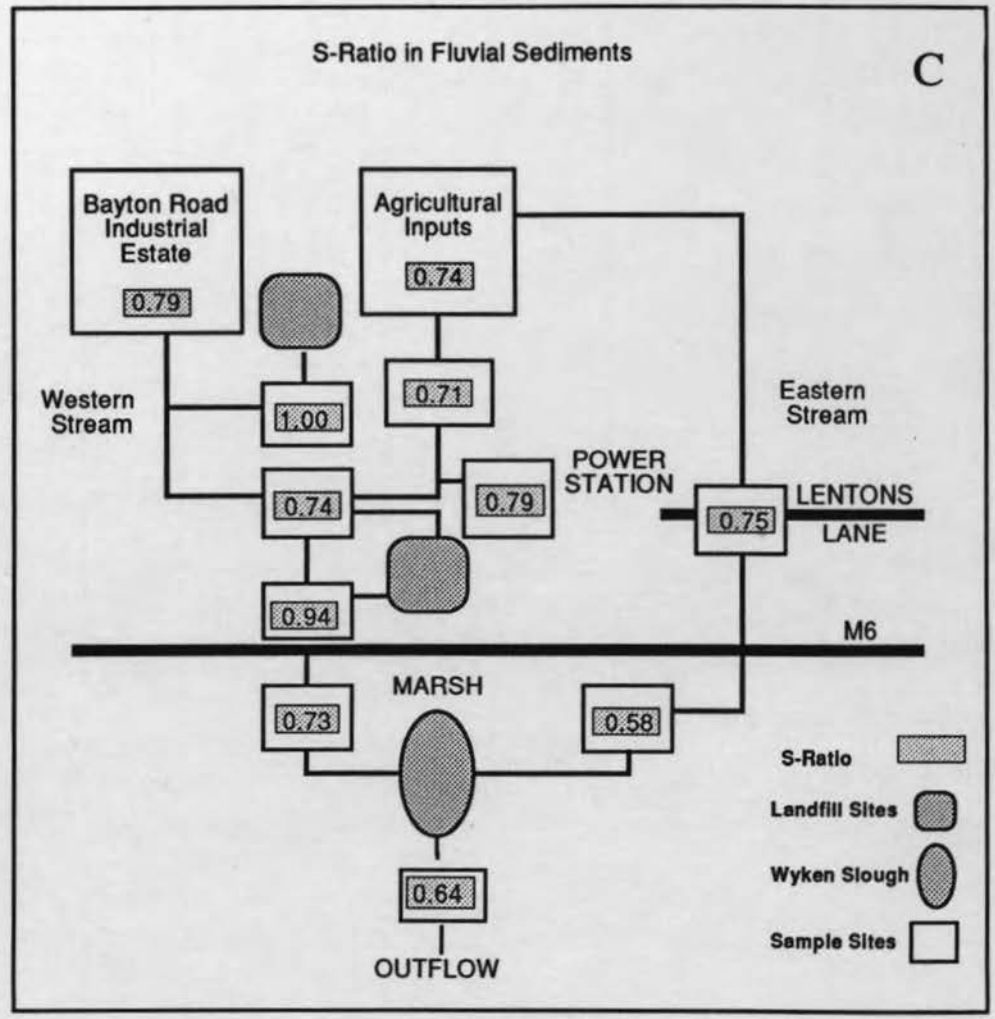
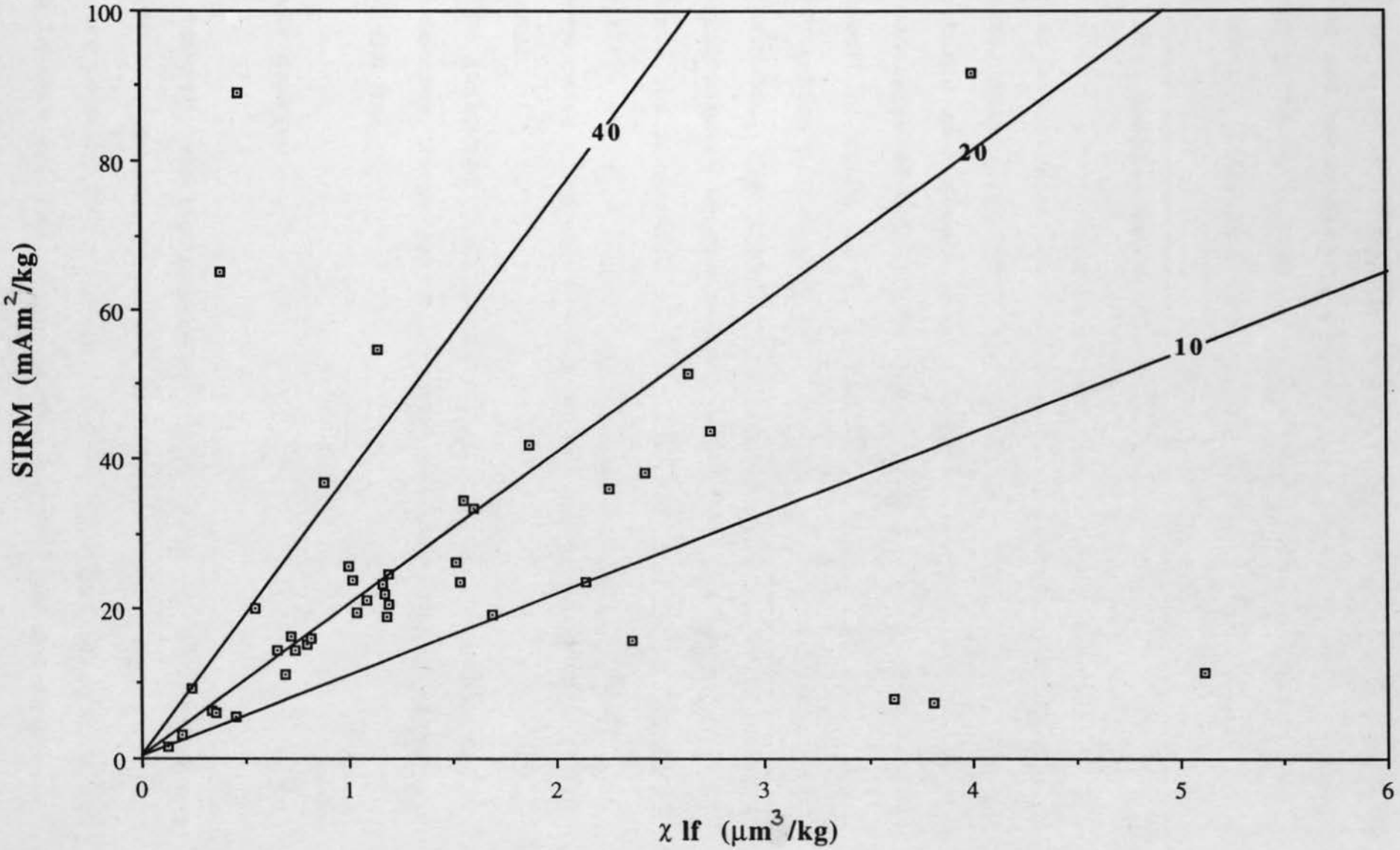

S-Ratio in Fluvial Sediments
C
Bayton Road Industrial Estate
0.79
Agricultural Inputs
0.74
Western Stream
1.00
0.71
Eastern Stream
POWER STATION
0.74
0.79
0.75
LENTONS LANE
0.94
M6
MARSH
0.73
0.58
0.64
OUTFLOW
S-Ratio
Landfill Sites
Wyken Slough
Sample Sites

Fig 6.14 Scattergram of χlf against SIRM for stream bed sediments



Chapter 2.10.1e). There are a few points which lie between 20 and 40 and these may represent magnetic grains associated with larger particle size since these generally have higher SIRM and lower χ_{lf} values (Thompson & Oldfield, 1986).

6.4. Soil samples from Wyken Slough

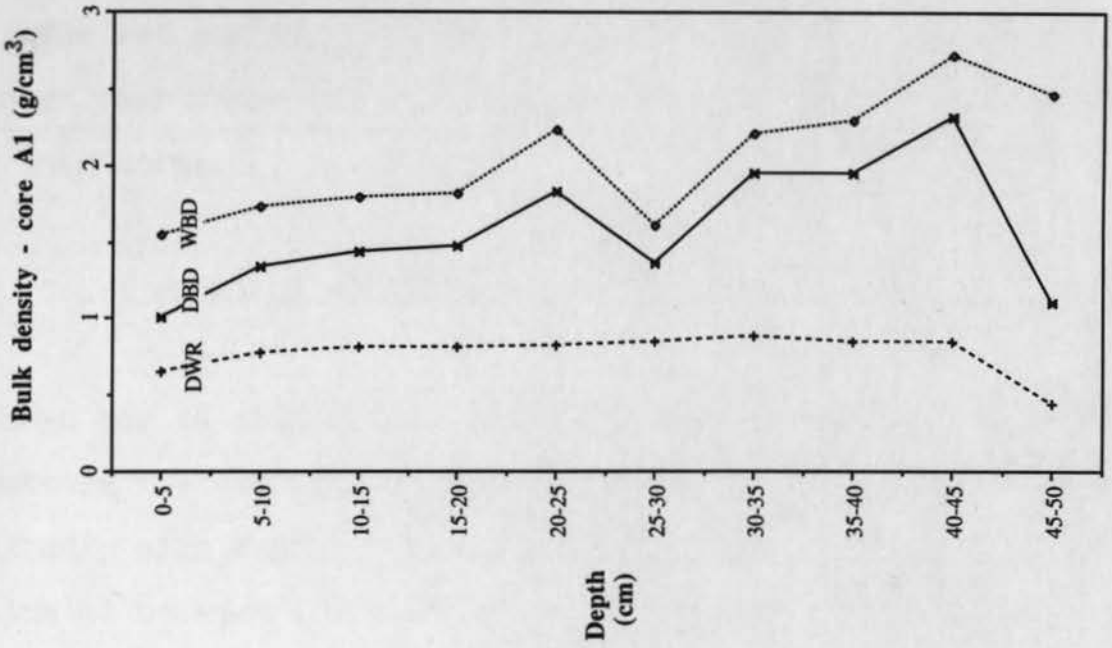
Chapter 2 justified the analysis of catchment soils for two reasons; their importance as a sink of heavy metals and their importance as a source of sediment to the lake. If the soils are contaminated with heavy metals then the erosion and transport of soils into the lake will enhance the concentration of heavy metals. If they are not significantly contaminated, then their incorporation into the lake sediments can dilute metal concentration. This section therefore examines the properties of the soils to both assess their chemistry, but also to provide a fingerprint whereby their importance as a source of sediment to the lake can be assessed.

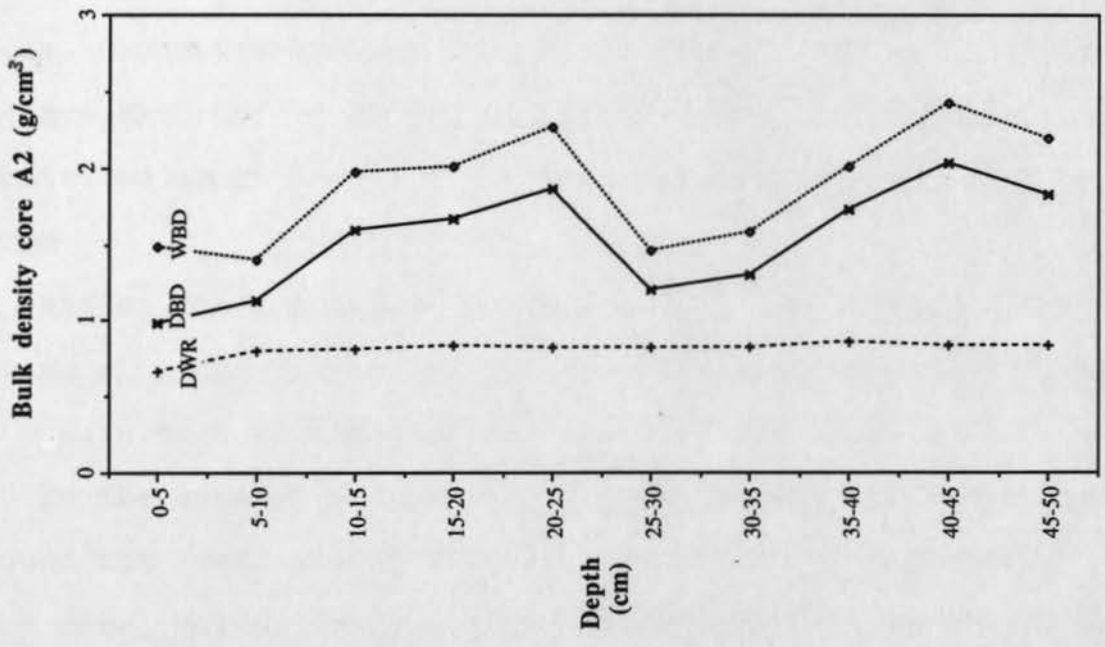
The following section is divided into four subsections, bulk density, heavy metals, mineral magnetic measurements and P, Fe and Mn.

i. Bulk density

Bulk density data are presented in Fig 6.15. In both cores wet and dry bulk density increases slowly with depth apart from a decrease between 25 and 30 cm depth in core A1 and between 25 and 35 cm in core A2. The ratio between the dry and wet bulk

Fig 6.15 Downcore trends in soil bulk density
a. Core A1 b. Core A2





density increases slightly downprofile in both cores, but then remains at about 0.8 down to the basal sample in core A2. The sample at the base of core A1 decreases sharply to 0.45.

The wet and dry bulk densities for core A1 are generally higher than those for A2, but the dry / wet ratios are similar in both cores.

ii. Total chemical extraction for heavy metals.

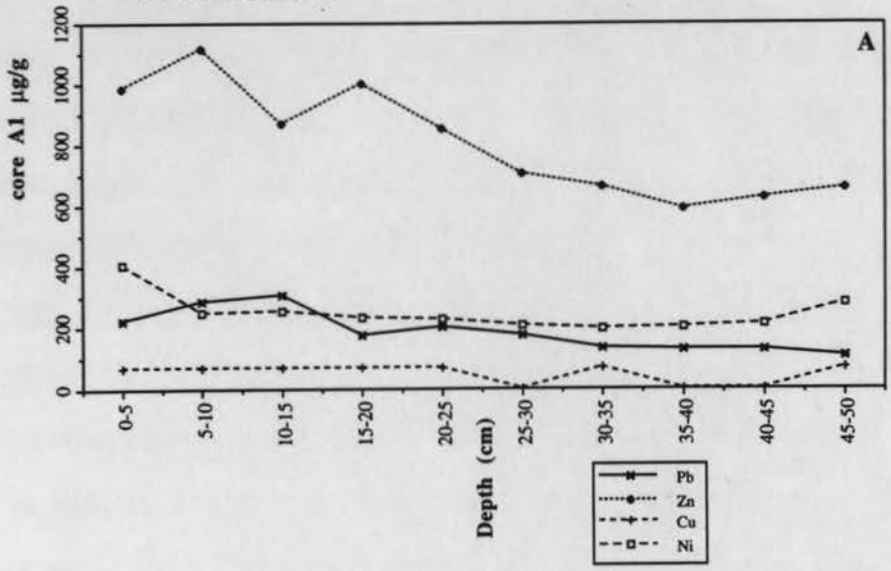
Except for Zn (Fig 6.16), where concentration decreases with depth in the profile, heavy metal concentrations do not vary markedly with depth. The highest value for Zn in core A1, at a depth of between 5 and 10 cm is 1100 $\mu g\ g^{-1}$, which decreases to 600 $\mu g\ g^{-1}$ towards the bottom of the core. The highest value in core A2 is 1300 $\mu g\ g^{-1}$ at a depth of between 10 and 15 cm, this also decreases to 600 $\mu g\ g^{-1}$ at the bottom of the core.

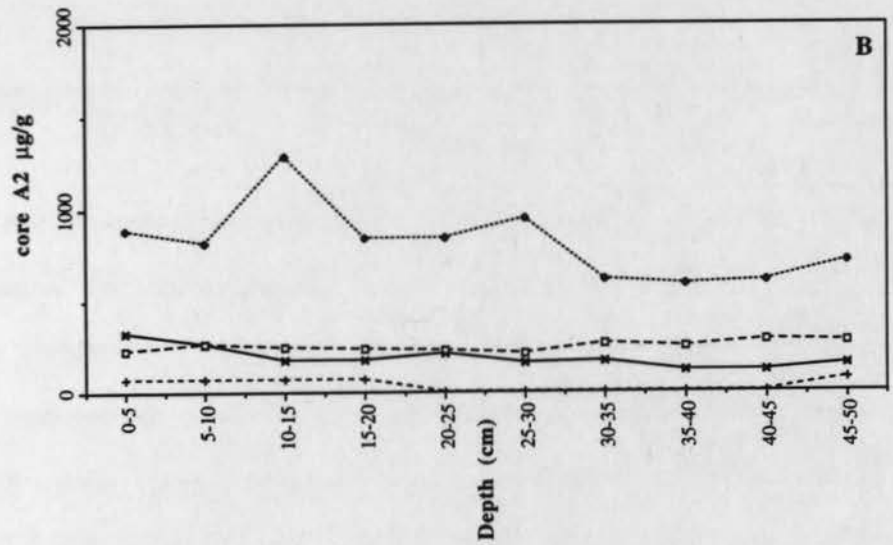
Pb declines slightly in concentration in both of the soil cores. Highest values of 300 (10-15 cm) and 326 $\mu g\ g^{-1}$ (0-5 cm) are recorded in A1 and A2 respectively. These values decline to about 110 $\mu g\ g^{-1}$ in the lower samples for both cores.

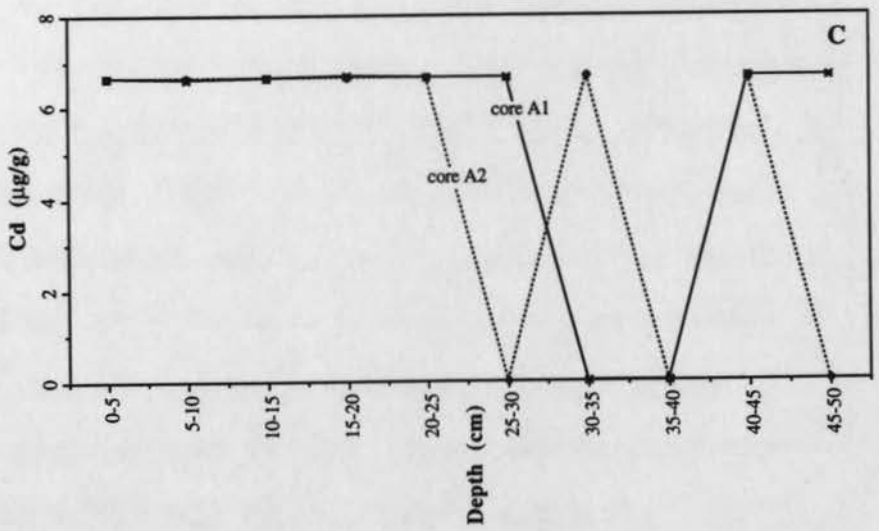
Whilst the top sample in core A1 has a Ni concentration of 400 $\mu g\ g^{-1}$, the values for the rest of this core and for core A2 remain at a fairly constant level of 200 $\mu g\ g^{-1}$.

In the case of both Cu and Cd, concentrations fluctuate around the lower limits of detection in the bottom half of each core. Values for Cd reach a maximum of 6.6 $\mu g\ g^{-1}$ in both cores, whereas values for Cu reach a maximum of 66 $\mu g\ g^{-1}$.

Fig 6.16 Downcore trends in soil heavy metal content
a. core A1, Pb, Zn, Cu and Ni b. core A2 Pb, Zn, Cu and Ni
c. cores A1 and A2, Cd







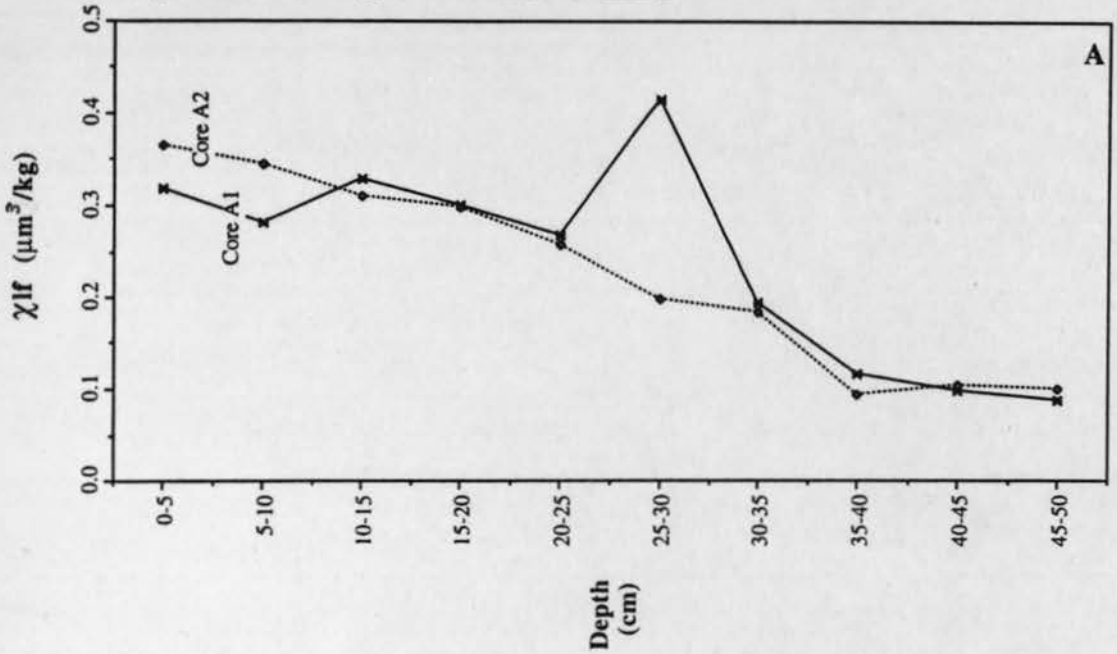
Concentrations of heavy metals are generally higher in the topsoil than in the subsoil. However, Cd concentrations are at the limits of detection of the instrument and show very little variation in either core if it is detected at all. Ni concentrations vary very little in either core, although they are slightly higher in the uppermost samples of core 1.

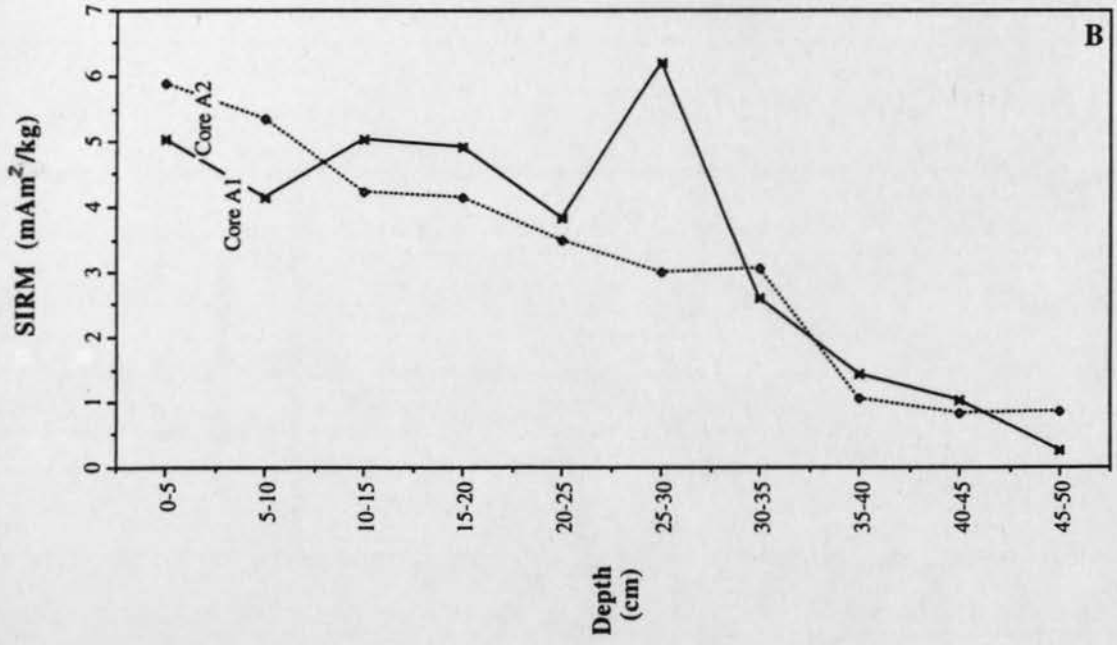
Section 6.7.2 summarises the data from the Wyken Slough and includes a comparison of the maximum heavy metal concentrations from each component and also the F values from each component.

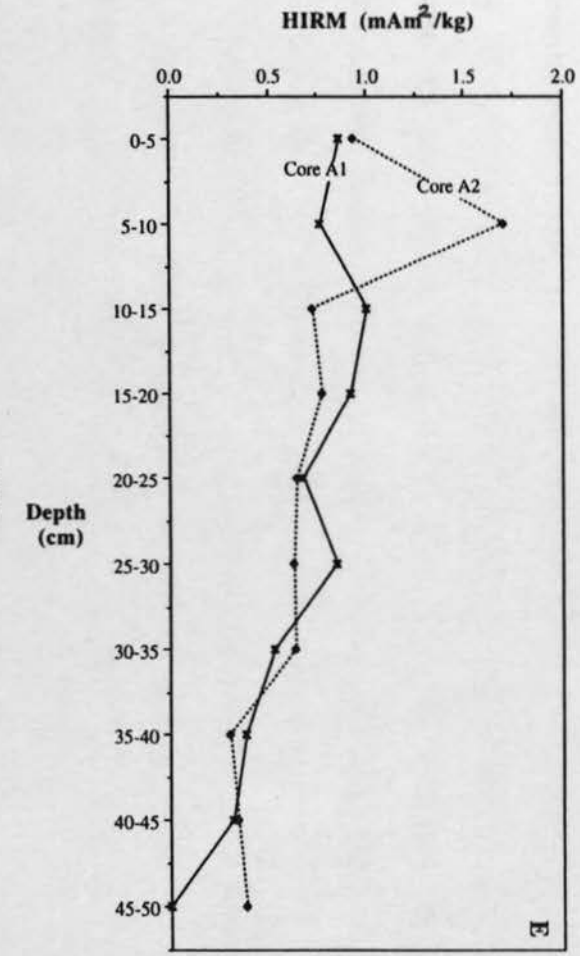
iii. Mineral magnetic properties of the soils.

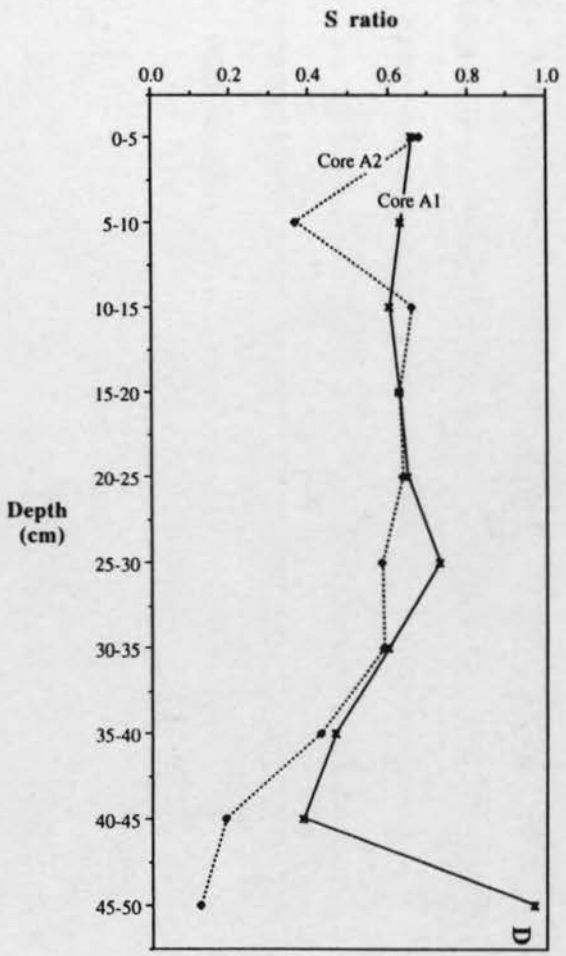
Both χ_{lf} and SIRM decrease down the profile (Figs 6.17 a and b), although there is an area of high values in both parameters at a depth of between 25 and 30 cm in core A1 where values for χ_{lf} exceed 0.4 μm^3 kg^{-1} and SIRM reaches 6.2 mAm^2 kg^{-1}. Values for both parameters become constant at depths of between 35 and 50 cm in core A2, with SIRM at 1 mAm^2 kg^{-1} and χ_{lf} at 0.1 μm^3 kg^{-1}. χ_{fd}, the S-ratio and HIRM are presented on Figs 6.17 c - e, the values for χ_{fd} are low (less than 20 nm^3 kg^{-1}) at the top of each soil core, increasing to just less than 30 nm^3 kg^{-1} at 6cm depth in both cores and then decreasing to less than 1 nm^{-3} kg^{-1} at the bottom of each core. The S-ratio and HIRM are mirror images of one another but both have fairly high values, S-ratio reaching almost 1 in core A1 and HIRM reaching 1 in both cores in the upper samples. Similar high values in the upper portions of the cores may indicate a mixture of ferrimagnetic and

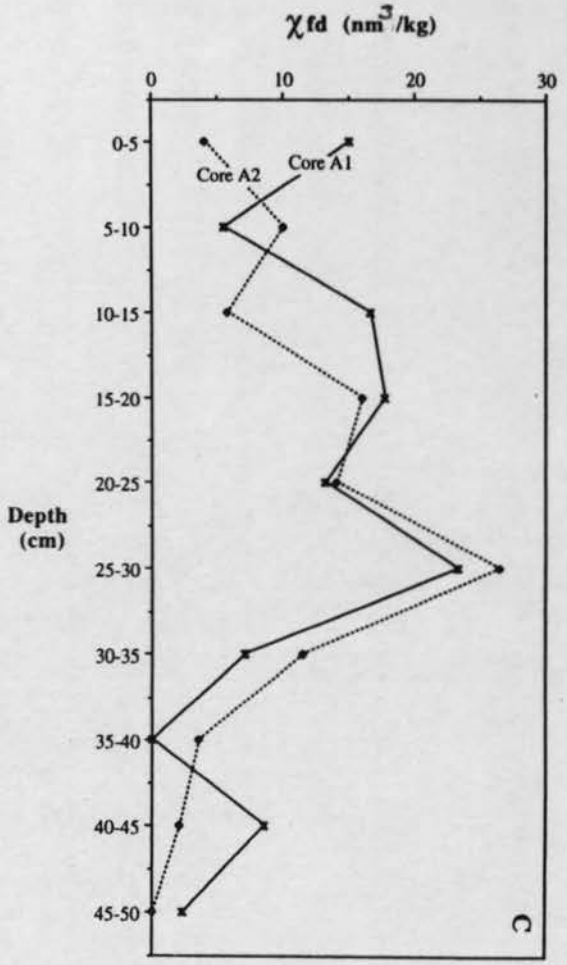
Fig 6.17 Downcore trends in soil mineral magnetic characteristics for both cores a. χlf b. SIRM c. χfd d. S ratio e. HIRM






HIRM (mAm²/kg)
0.0
0.5
1.0
1.5
2.0
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
Depth (cm)
Core A1
Core A2
E


S ratio
0.0
0.2
0.4
0.6
0.8
1.0
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
Depth (cm)
Core A2
Core A1
D


χfd (nm³/kg)
0
10
20
30
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
Depth (cm)
Core A2
Core A1
C

antiferromagnetic minerals in the soils of the Wyken Slough catchment.

χ_{lf} and SIRM were used to construct the scattergram shown in Fig 6.18 which combined the results from both cores. Superimposed on the scattergram are lines of gradient representing ratios of 10:1 and 20:1. The majority of the points lie between these ratio lines which therefore represent antiferromagnetic MD grains (Thompson & Oldfield, 1986; see also Fig 4.16 and Chapter 2.10.ie). The scattergrams discriminate between 3 groups of samples; those with higher χ_{lf} and SIRM, those with low χ_{lf} and SIRM and three samples in between these two groups. Since Thompson & Oldfield, 1986, state that topsoils exhibit magnetic 'enhancement', then the first group represent topsoil, the last group represent subsoil and the group of intermediate characteristics may represent a transition between the topsoil and subsoil as indicated on Fig 6.18.

iv. P, Fe and Mn

Profiles for P concentration are shown in Fig 6.19 a. The highest concentration was found in the top sample of core A1 with a value of 445 $\mu g\ g^{-1}$. The concentration of P in the top sample of core A2 was found to be 280 $\mu g\ g^{-1}$. The amount of P declines from these levels to the basal samples where they were 50 and 70 $\mu g\ g^{-1}$ in cores A1 and A2 respectively.

Topsoil contains the highest concentrations of P and apart from sample 7 in core 1, the subsoils contain the lowest concentrations.

Fig 6.18 Scattergram of χlf against SIRM for both soil cores

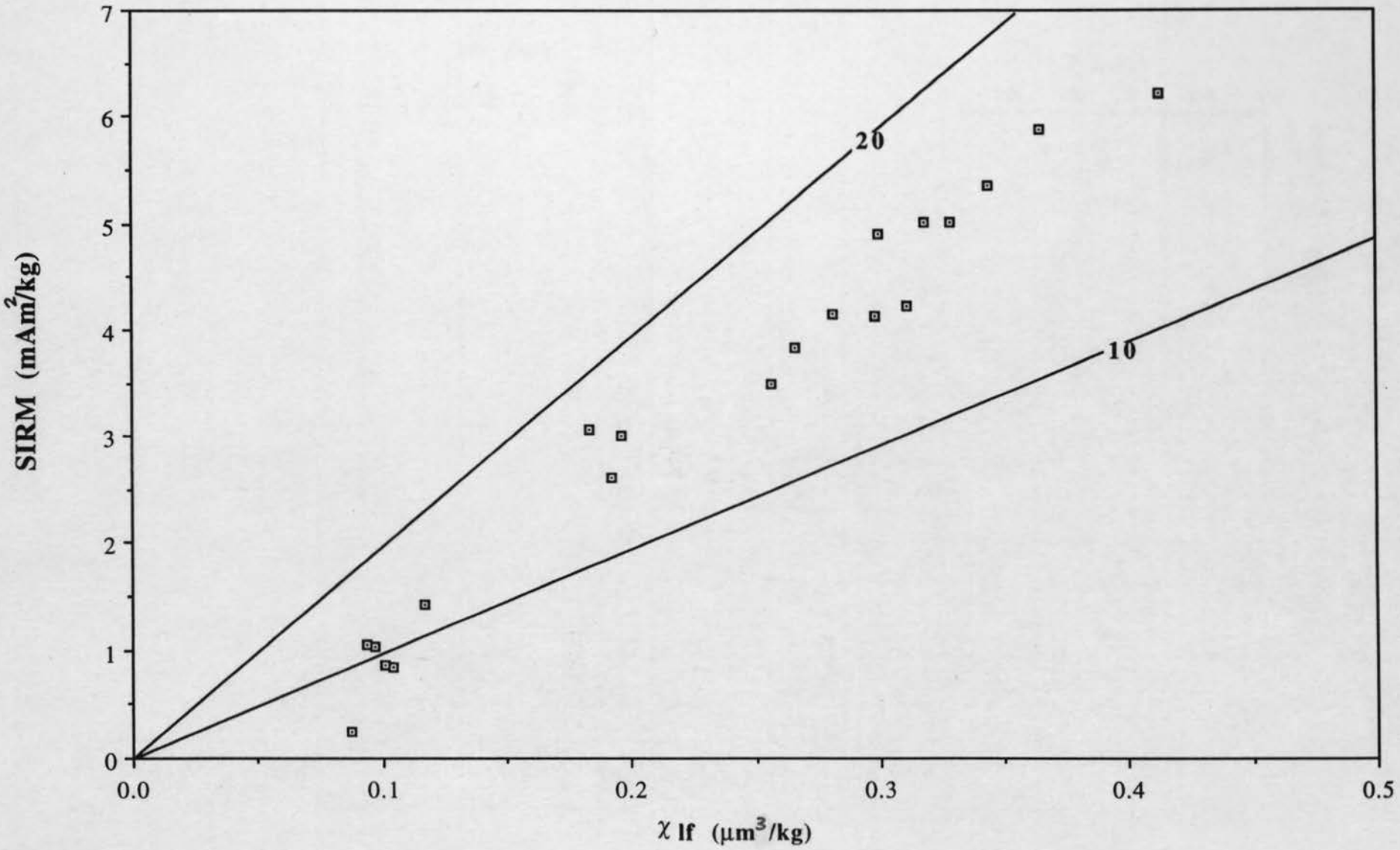
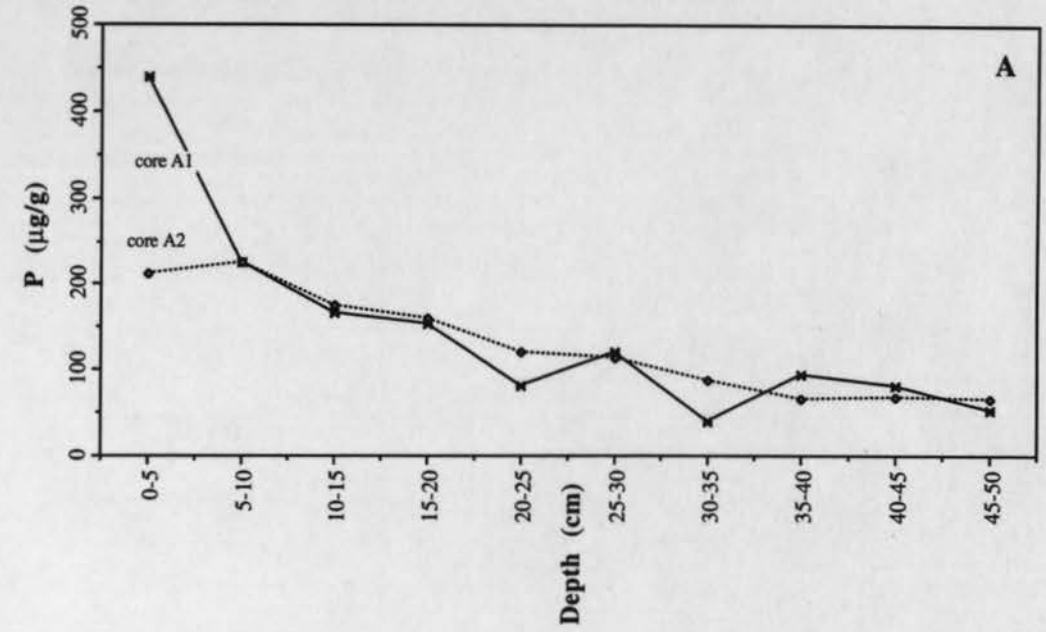
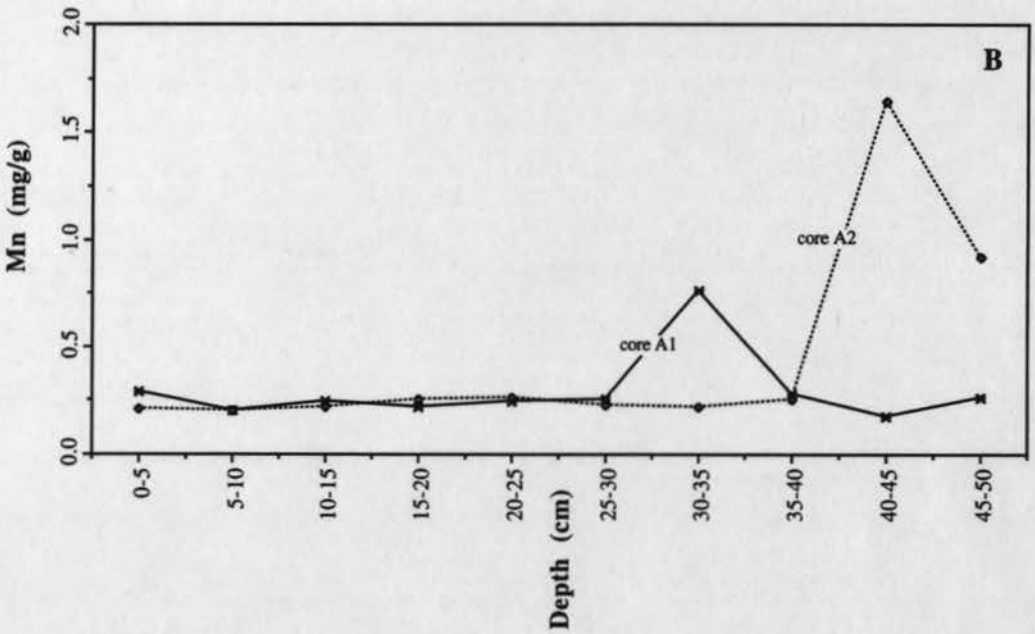
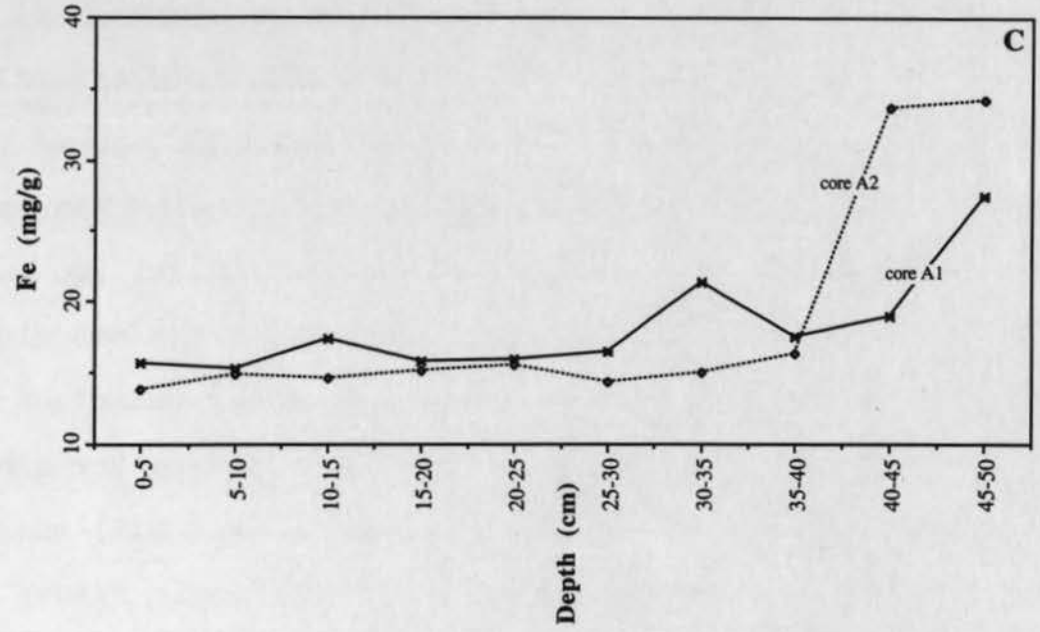
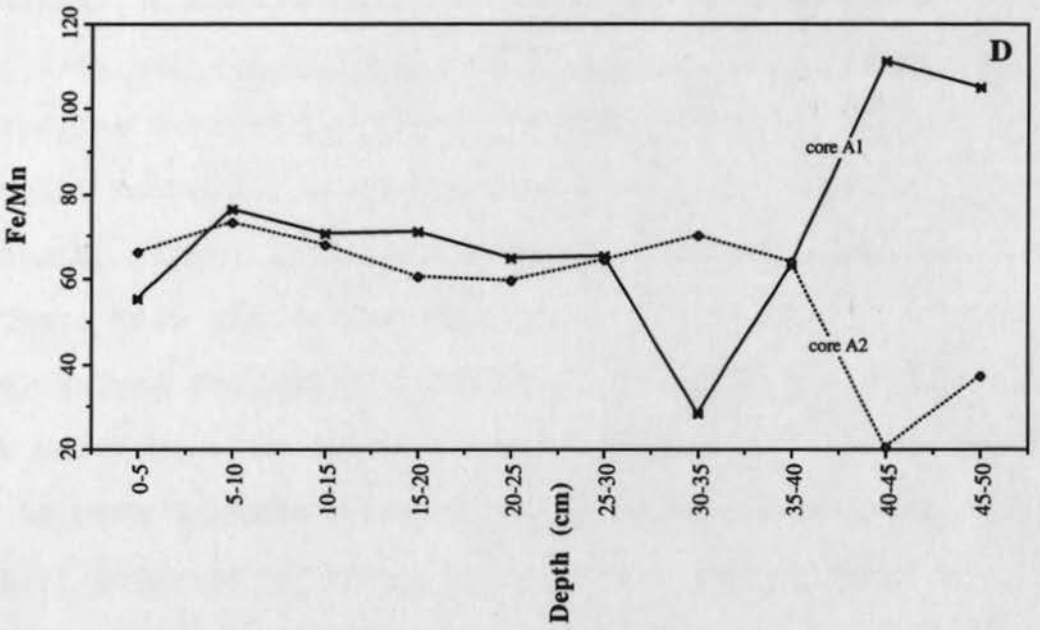


Fig 6.19 Downcore trends in soil P, Mn, Fe and Fe / Mn
a. P b. Mn c. Fe d. Fe / Mn






C
Fe (mg/g)
10
20
30
40
core A2
core A1
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
Depth (cm)


D
Fe/Mn
20
40
60
80
100
120
core A1
core A2
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
Depth (cm)

The sampling site (Fig 2.11 a) retained ridge and furrow features showing that it has probably remained relatively undisturbed since medieval times, although the history of the field is unknown. It is unimproved pasture used for grazing animals, therefore one source of nutrients to the soil is from animal manure. Pelleted inorganic fertilisers or organic manures can be applied to grassland, but whether this has been carried out is unknown. The main source of heavy metals is probably the atmosphere and more particularly, the M6 motorway which dominates the site (Chapter 3, Plate 1). At its closest, the motorway passes within 200 m of the soil sampling locations (Fig 2.11 b) and in a study of the deposition of heavy metals alongside the M6 motorway in the north of England, Johnston & Harrison (1984) found that whilst the majority of metals were deposited within 50 m of the carriageway, a substantial amount, up to twice background in some cases, was deposited up to 250 m from the carriageway. The profiles described above therefore reflect a combination of natural pedogenic processes, the cycling of chemical elements by plants (Mattigod & Page, 1983) and airborne pollutants from the M6 motorway.

Fe, Mn and Fe / Mn are shown in Figs 6.19 b - d and are fairly constant with depth until 25 - 30 cm in core 1 and 35 - 40 cm in core 2 where concentrations of Fe and Mn rise slightly. Redox conditions are therefore stable until conditions become anaerobic lower in the core.

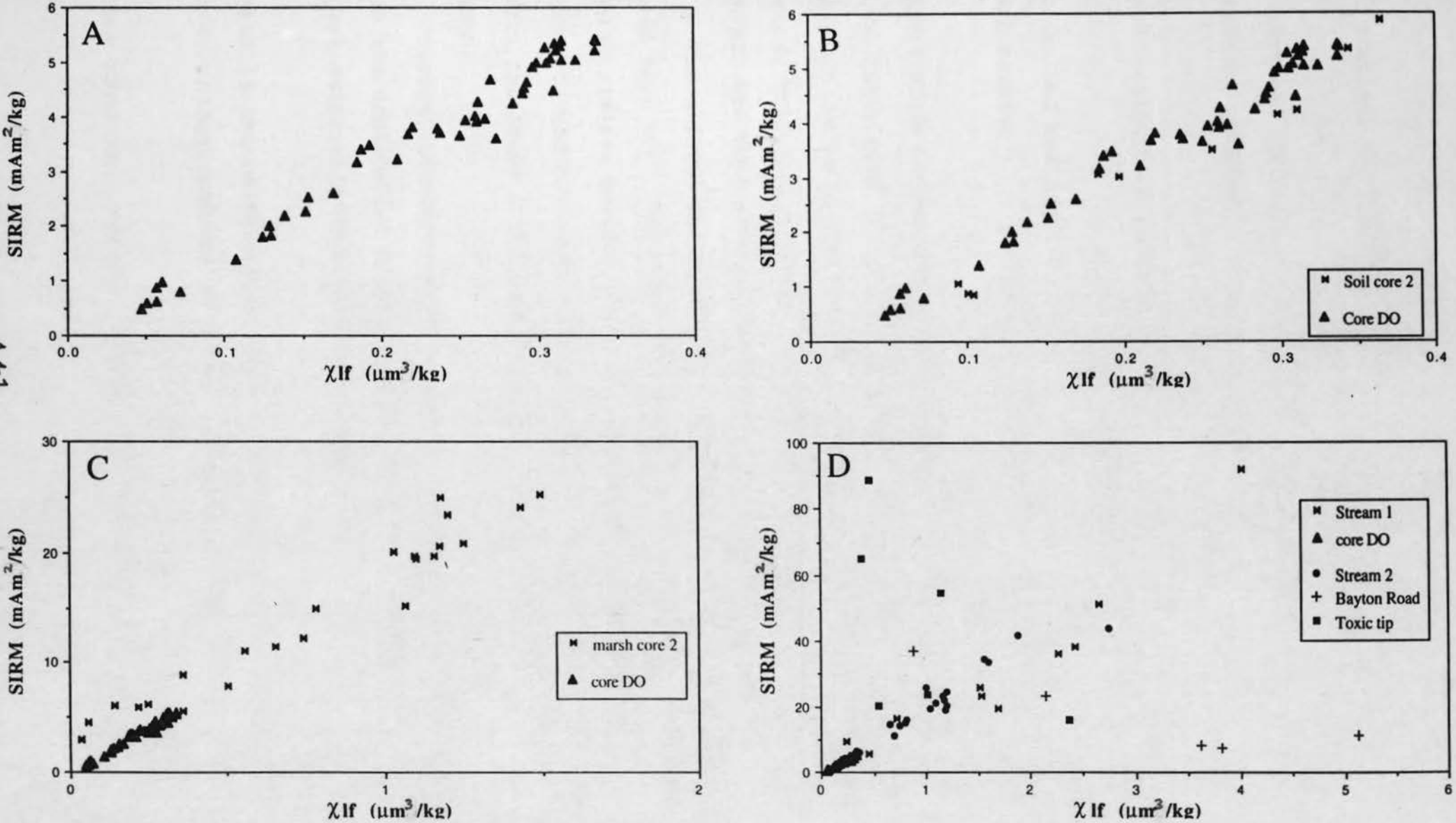
6.5 Sediment sources to Wyken Pool using mineral magnetic characteristics

One of the objectives of this study was to identify the role of the drainage basin in the sediment delivery process. A means of assessing this is to attempt to identify the source of the sediments in Wyken Pool.

One of the reasons discussed in Chapter 2.10 (ie) for the measurement of mineral magnetic characteristics was that it could be used to aid in the tracing of sediment sources by characterisation of solid deposits such as soils and fluvial substrates and their comparison with the signal obtained from the lake sediments. Chapter 4.2.5 c justified the use of scattergrams to characterise the solid deposits for examining sediment source tracing. These scattergrams utilised measurements of χ_{lf} and SIRM which have been used in many studies to identify source materials (Oldfield *et al.*, 1979; Walling *et al.*, 1979; Snowball & Thompson, 1992).

Fig 6.20 shows scattergrams of χ_{lf} against SIRM for lake core DO from Wyken Pool. Superimposed on these are scattergrams for the soils, marsh and stream sediments. These show reasonable relationships between the soils, the marsh sediments, the eastern and the western stream sediments, but little relationship with the bed sediments of either the toxic tip or the Bayton Road sediments. The lake sediments therefore probably represent a complex mixture of catchment derived sources in which there does not appear to be one dominant source.

Fig 6.20 Scattergrams of χ_{lf} against SIRM
a. core DO from Wyken Pool b. core DO and soil core A2 c. core DO and Marsh core 2
d. core DO, stream 1, stream 2, Bayton Road and Toxic Tip bed sediments



6.6 Statistical analysis

Statistical analysis was carried out on the individual catchment components as listed below:

Marsh sediments : surface samples

2 marsh cores both separately and together

Stream bed sediments

Soil samples : 2 cores both separately and together

Descriptive statistics, skewness, kurtosis and correlation were calculated on all the above data sets and regression was carried out on selected data as explained in section 6.5 iii below. Principal Component Analysis (PCA) was also carried out on all the data sets listed above.

The objectives of statistical analysis and the methodology used have been introduced in Chapter 4.3. Normalisation of the data, similar to that found in the two lakes, (Chapters 4.3 and 5.3) did not consistently improve the distribution of the data and hence subsequent analysis was carried out on raw data.

Several questions were set up in Chapter 2.13 with respect to the application of statistical analysis, the two of particular relevance to this Chapter are:

What is the relationship between the catchment components at Wyken Slough and the sediment deposited in the lake?

How consistent are the results from the four lake cores?

The data sets from Chapters 5 (the Wyken Pool sediments) and 6 (the catchment components) have therefore been integrated in order to address these two questions and analysed using PCA.

The results of statistical analysis is divided into two sections, firstly covering descriptive statistics, correlation and regression and secondly a description of results obtained from PCA.

a. Descriptive statistics, correlation and regression

This section is divided into three parts in order to address the same questions as detailed in Chapter 4.3 a.

Mean, minimum and maximum values of catchment components are given in Table 6.5. Table 6.6 compares the maximum concentrations of heavy metals between Swanswell and Wyken Pools and the Wyken Slough catchment components.

i. The relationship between mineral magnetic parameters in samples from Wyken Slough.

Correlation matrices for the magnetic parameters show a similarly high level of interdependance as was found in the lake sediments from both sites. Table 6.7 illustrates this with a correlation matrix taken from Marsh core 2. The correlation between measured parameters is high, whilst the correlation between derived characteristics is less significant and that between measured and derived parameters is mostly significant at the 99.9% level. Correlation between

Table 6.5 Summary descriptive statistics of sediments from Wyken Slough.

a.) Marsh cores

Variable	Mean	Minimum	Maximum
χ_{lf} [1]	0.63	0.0	1.5
χ_{fd} [2]	10.72	0.0	57.4
SIRM [3]	11.13	2.9	25.2
S ratio	0.71	0.5	1.0
HIRM [3]	1.54	0.0	4.2
DBD [4]	0.39	0.1	1.0
WBD [4]	0.71	0.1	1.4
DWR	0.47	0.1	0.8
Fe [5]	24.64	16.6	34.4
Mn [5]	1.14	0.5	3.4
Fe/Mn	28.78	8.1	43.4
Cd [6]	8.41	0.0	51.7
Pb [6]	157.88	49.1	1952.4
Ni [6]	91.18	15.1	417.2
Zn [6]	563.79	137.6	2880.4
Cu [6]	90.28	19.7	295.3
P [6]	529.73	0.0	1719.0

b.) Soil cores

χ_{lf} [1]	0.23	0.1	0.4
χ_{fd} [2]	10.12	0.0	26.5
SIRM [3]	3.32	0.3	6.2
S ratio	0.56	0.1	1.0
DBD [4]	1.55	0.56	2.43
WBD [4]	1.96	1.4	2.7
DWR	0.79	0.4	0.9
Fe [5]	18.48	13.8	34.2
Mn [5]	0.37	0.2	1.6
Fe/Mn	64.77	20.5	111.1
Cd [6]	4.98	0.0	6.7
Pb [6]	184.66	106.2	326.1
Ni [6]	246.14	192.2	405.9
Zn [6]	808.43	584.4	1282.0
Cu [6]	39.85	0.0	66.6
P [6]	137.02	38.4	439.2

Units
[1] $\mu m^3\ kg^{-1}$
[2] $nm^3\ kg^{-1}$
[3] $mAm^2\ kg^{-1}$
[4] $g\ cm^{-3}$
[5] $mg\ g^{-1}$
[6] $\mu g\ g^{-1}$

Table 6.5 (continued)

c.) Stream bed sediments

Variable	Mean	Minimum	Maximum
χ_{lf} [1]	1.44	0.1	5.1
χ_{fd} [2]	28.55	0.0	56.0
SIRM[3]	25.96	1.5	91.7
S-ratio	0.77	0.58	1.0
HIRM[3]	2.6	0.0	5.82
Fe	35.53	17.6	84.74
Mn	0.91	0.35	2.0
Fe/Mn	48.0	10.1	97.02
Cd[6]	4.57	0.0	26.0
Pb[6]	138.41	0.0	533.3
Ni[6]	46.44	0.0	150.4
Zn[6]	369.09	0.0	1804.1
Cu[6]	16.86	0.0	96.8
P[6]	359.46	96.8	604.2

Units
[1] $\mu m^3\ kg^{-1}$
[2] $nm^3\ kg^{-1}$
[3] $mAm^2\ kg^{-1}$
[4] $g\ cm^{-3}$
[5] $mg\ g^{-1}$
[6] $\mu g\ g^{-1}$

Table 6.6 Maximum concentrations for heavy metals from Wyken and Swanswell Pools and the Wyken Slough catchment ($\mu g\ g^{-1}$)

	1	2	3	4	5	6
Zn	3600	2200	7000	1300	2800	2200
Ni	140	210	800	400	420	310
Cu	600	200	340	70	300	470
Pb	550	700	210	330	230	300
Cd	60	30	15	7	50	20

1. Swanswell Pool sediments (n = 176)
2. Wyken Pool sediments (n = 237)
3. Wyken Slough stream bed sediments (n = 42)
4. Wyken Slough soils
5. Wyken Slough marsh core samples (n = 53)
6. Wyken Slough surface samples (n = 20)

χ_{fd} and all other mineral magnetic characteristics is generally the least significant.

Table 6.7 Correlation between mineral magnetic parameters from Marsh core 2 (n=24, critical R = 0.42).

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-RATIO
χ_{lf}	-						
χ_{hf}	0.9999**	-					
χ_{fd}	0.6372**	0.6264**	-				
SIRM	0.9752**	0.9752**	0.5877*	-			
IRM	0.9785**	0.9788**	0.5673*	0.9923**	-		
HIRM	0.8734**	0.8725**	0.5933**	0.9288**	0.8757**	-	
S-ratio	0.6801**	0.6802**		0.6558**	0.7288**		-

** denotes significance of 99.9%

* denotes significance of 99%

ii. The relationship between heavy metals in the Wyken Slough samples.

There is a high correlation between the heavy metals in certain of the catchment components. Tables 6.8 and 6.9 present a correlation matrix of heavy metal concentrations from all the individual catchment components. In the case of

Table 6.8 Correlation between heavy metals in marsh samples

a. Marsh surface samples (n=20, critical R=0.4438 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.8601**	-			
Zn	0.8869**	0.9032**	-		
Pb	0.6713**	0.6817**	0.7009**	-	
Cu	0.8524**	0.8980**	0.8654**	0.7340**	-

b.) Combined marsh cores (n=53, critical R=0.273 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.9257**	-			
Zn	0.8371**	0.7717**	-		
Pb	0.7559**	0.7045**	0.8013**	-	
Cu	0.8950**	0.8233**	0.9095**	0.8480**	-

c.) Marsh core 1 (n=29, critical R=0.365 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.6767**	-			
Zn	0.6239**		-		
Pb	0.3800**		0.7603**	-	
Cu	0.7047**	0.4404*	0.8262**	0.8499**	-

d.) Marsh core 2 (n=24, critical R=0.41 at 99%

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.9021**	-			
Zn	0.6365**	0.6959**	-		
Cu	0.727**	0.6363**	0.5887*		-

No correlation with Pb

Table 6.9 Correlation between heavy metals in soils and stream bed sediments

a.) Combined soil cores (n=20, critical R=0.4438 at 99%)

	Cd	Ni	Zn	Pb	Cu
Zn			-		
Pb			0.5364*		-
Cu			0.5279*		-

No correlation with Cd or Ni

---

b.) Soil core A1 (n=10, critical R=0.6319 at 99%)

	Cd	Ni	Zn	Pb	Cu
Zn			-		
Pb			0.7696*	-	

No correlation with Cd, Cu or Ni

---

c.) Soil core A2, no correlations

---

d.) Stream samples (n=41, critical R=0.3044 at 99%)

	Cd	Ni	Zn	Pb	Cu
Cd	-				
Ni	0.8453**	-			
Zn	0.5280**	0.4591*	-		
Pb	0.4138*		0.4607*	-	
Cu	0.7771**	0.7172**	0.5503**	0.4889**	-

---

the marsh surface samples (Table 6.8), all heavy metals correlate at the 99.9% significance level with each other. Taking both marsh cores together, the same is true but, taken individually, Ni does not correlate with Zn or Pb in core 1 and Pb does not correlate with any other metal in Core 2. The soil cores taken together (Table 6.9), indicate no correlation at all with Cd and Ni and only at the 99% significance level for the parameters which do correlate. Soil core A1 shows correlation between Pb and Zn only at the 99% significance level and there are no heavy metals which correlate in core A2. Most metals intercorrelate in the stream samples, the one exception being Ni with Pb.

Correlation between the heavy metals in samples from Wyken Slough are thus inconsistent, which seems to preclude the use of individual heavy metals as a predictive tool.

iii. Correlation and regression between heavy metals concentration and mineral magnetic parameters.

Tables 6.10 and 6.11 present correlation matrices of heavy metals with magnetic parameters. The marsh grid samples show correlations at the 99% significance level with Cu only. Marsh cores taken both together (Table 6.10) correlate mainly with the derived parameters of χ_{fd}, HIRM and the S-ratio. Taken separately in the case of core 1, most metals correlate with most magnetic parameters except HIRM. Core 2, however, does not exhibit significant correlation with Cd, Ni or Pb, but Zn and Cu correlate with most magnetic parameters. Both soil cores (Table 6.11), show no significant correlation between Cu

Table 6.10 Correlations between heavy metals and mineral magnetic parameters in marsh sediments

a.) Marsh surface samples (n=20, critical R=0.4438 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cu	0.5722*	0.5694*		0.5379*	0.5224*	0.5722*	

No correlation with Cd, Ni, Zn or Pb

---

b.) Combined marsh cores (n=53, critical R=0.273 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd			0.7989**				0.4808**
Ni			0.7416**				0.3411*
Zn			0.7433**				0.6032**
Pb			0.7907**			0.3859*	0.4989**
Cu			0.7802**			0.3390*	0.6343**

---

c.) Marsh core 1 (n=29, critical R=0.365 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.7019**			0.6817**	0.7522**		
Ni	0.5193**	0.6964**	0.6014**	0.6817**	0.5027*		
Zn	0.8164**	0.5157*	0.4770*	0.6561**	0.8166**		0.6051**
Pb	0.8652**	0.8606**	0.6949**	0.7141**	0.8605**		0.5962**
Cu	0.8109**	0.8147**	0.4973*	0.6288**	0.8322**		0.7651**

---

d.) Marsh core 2 (n=24, critical R=0.41 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Zn	0.7774**	0.7747**	0.4821*	0.8287**	0.8158**	0.7892**	0.5167*
Cu	0.5584*	0.5518*	0.5905*	0.4986*	0.5054*		

No correlation with Cd, Ni or Pb

Table 6.11 Correlation between heavy metals and mineral magnetic parameters in soils and stream bed sediments

a.) Combined soil cores (n=20, critical R=0.4438 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.5227*	0.5227*					
Zn	0.6166*	0.6166*		0.5942*	0.5913*		
Pb	0.7490**	0.7490**		0.7681**	0.6850**	0.7448**	

No correlation with Cu or Ni

---

b.) Soil core A1 (n=10, critical R=0.6319 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Pb						0.7617*	

No correlation with Cd, Ni, Zn or Cu

---

c.) Soil core A2 (n=10, critical R=0.6319 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Pb	0.8488**	0.8488**		0.8856**	0.7988*	0.7514*	

No correlation with Cd, Ni, Zn or Cu

---

d.) Stream samples (n=41, critical R=0.3044 at 99%)

	χ_{lf}	χ_{hf}	χ_{fd}	SIRM	IRM	HIRM	S-ratio
Cd	0.5519**						
Ni	0.5081**						
Cu	0.4314*						

No correlation with Pb or Zn

---

and Ni and magnetic parameters, whilst the remaining heavy metals correlate most significantly with measured parameters with the exception of Pb which correlates at the 99.9% significance level with HIRM. Taken individually, the soil cores only exhibit any significant correlation with Pb. Pb and Zn exhibit no significant correlation with any magnetic parameters in the stream samples; the remaining heavy metals correlating with χ_{hf} alone.

Regression analysis was carried out between heavy metals with magnetic parameters on marsh core A1, soil core A2 and the stream samples, as little correlation was shown in the other catchment components. This was to determine whether mineral magnetic measurements could be used to predict the levels of heavy metals in any of the catchment components. The samples selected were those which exhibited the highest correlation coefficients which are significant at the 99.9% significance level, such as Cd with χ_{lf} (0.7019**, see Table 6.10 c). The scattergrams are presented in Figs 6.21 to 6.23 with the associated values of explained variance and the regression equations. Chapter 4.3 aiii explains the theory behind the use of regression as a predictive tool.

R^2 values in Marsh core 1 are consistently higher for χ_{lf} than for SIRM; in the case of Pb with χ_{lf} 74.9% of the variance is explained. Ni has the lowest R^2 value with χ_{lf} at 27% and also the lowest with SIRM at 23.7%. In soil core 2, regression of Pb with χ_{lf} and SIRM both have R^2 values above 72%, but represent the only parameters with a significant relationship. Within the stream samples, the only significant correlation between heavy metals and magnetic parameters was

Fig 6.21 a. Regression, marsh core 1
i. Cd with χlf ii. Cd with SIRM

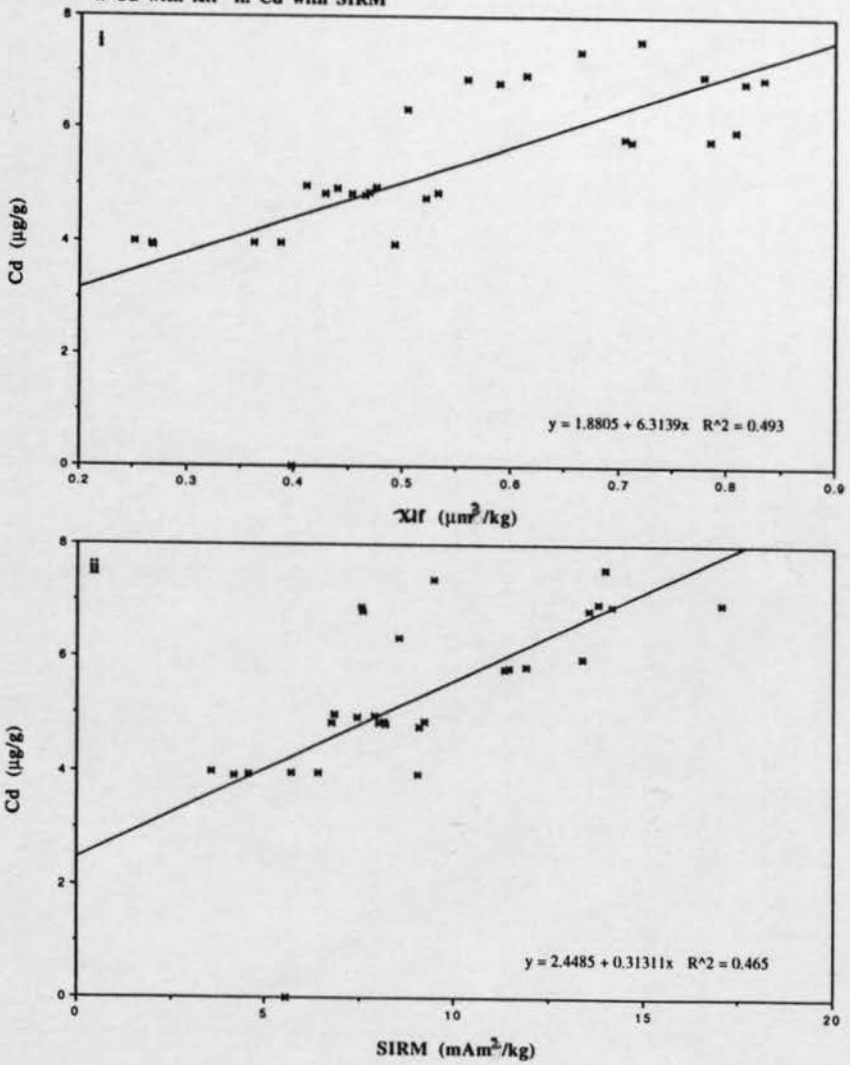


Fig 6.21 b. Regression, marsh core 1
i. Zn with SIRM ii. Zn with χlf

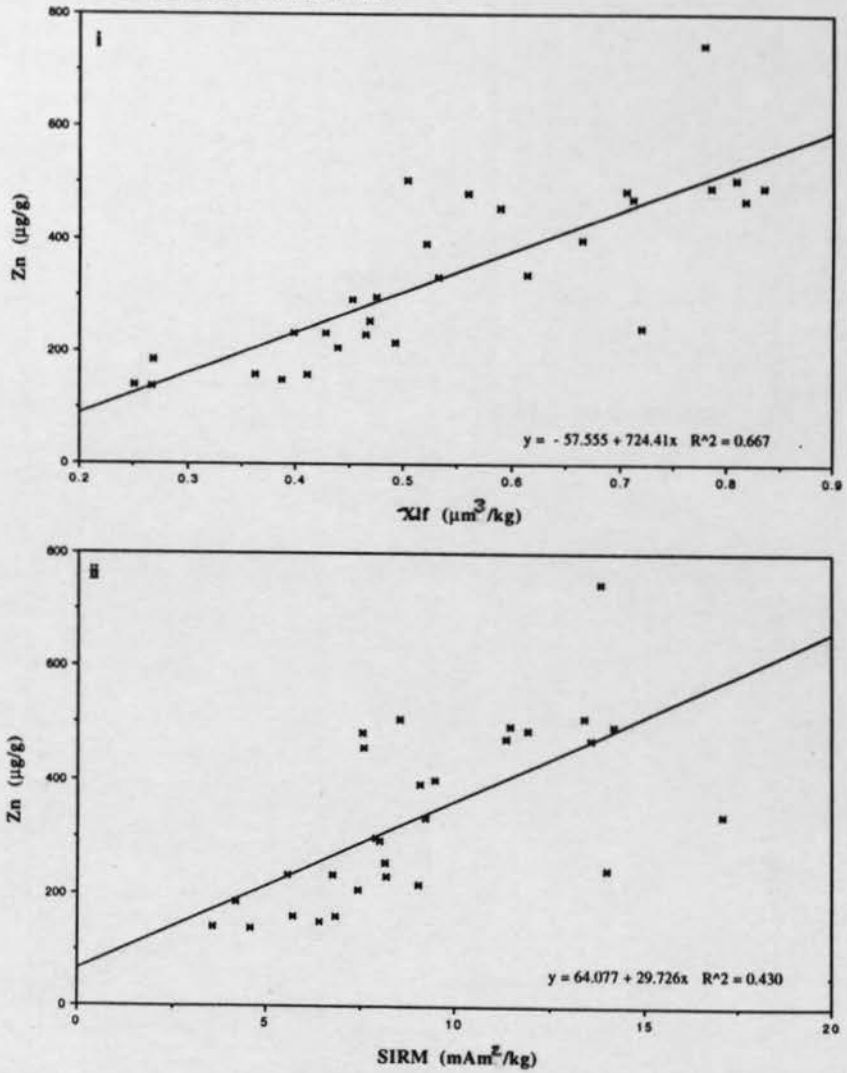
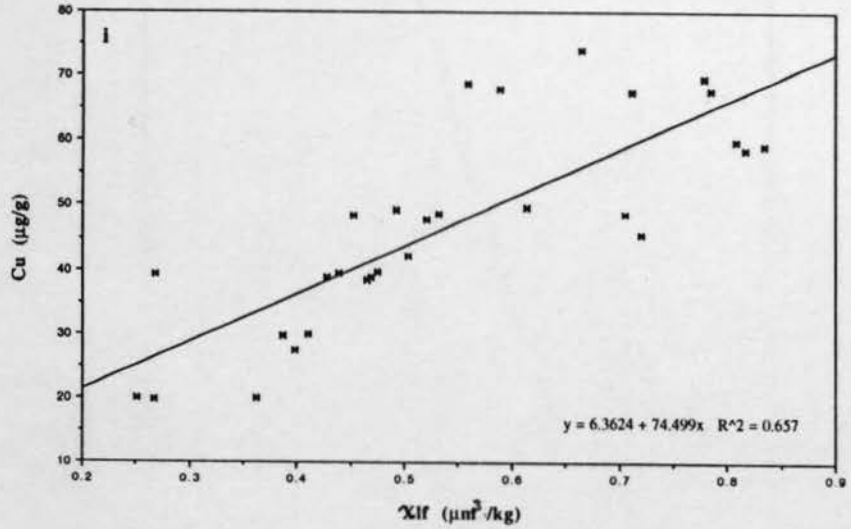


Fig 6.21 c. Regression, marsh core 1
i. Cu with χlf ii. Cu with SIRM



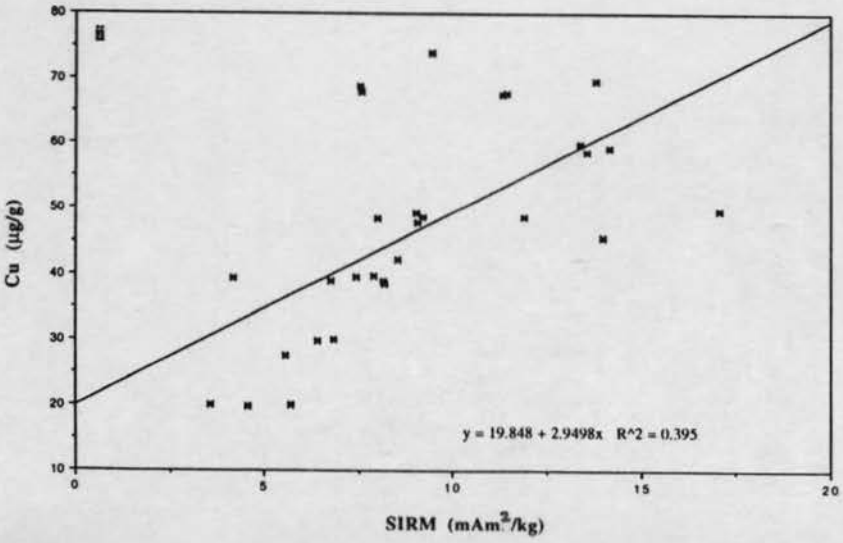
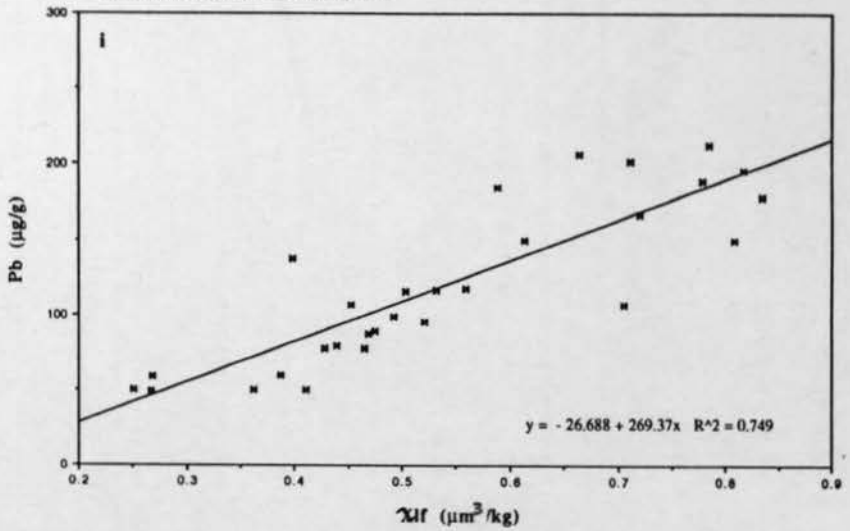


Fig 6.21 d. Regression, marsh core 1
i. Pb with χlf ii. Pb with SIRM



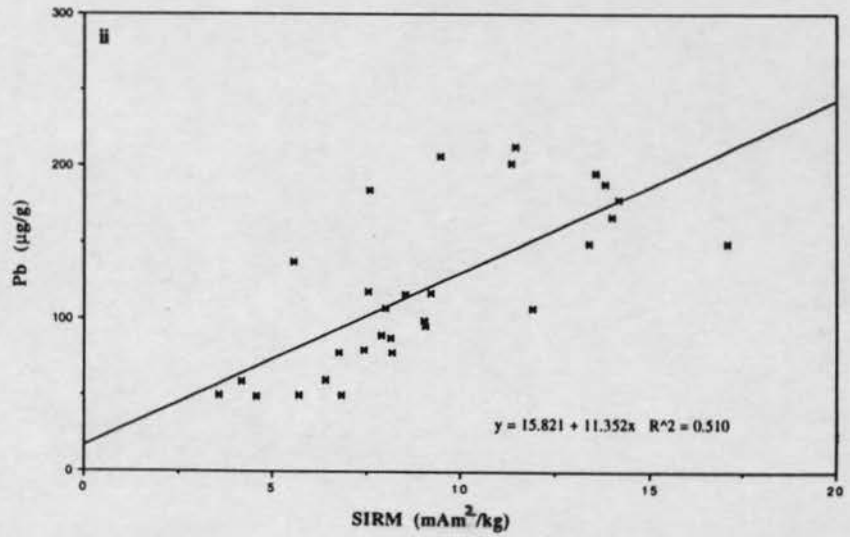
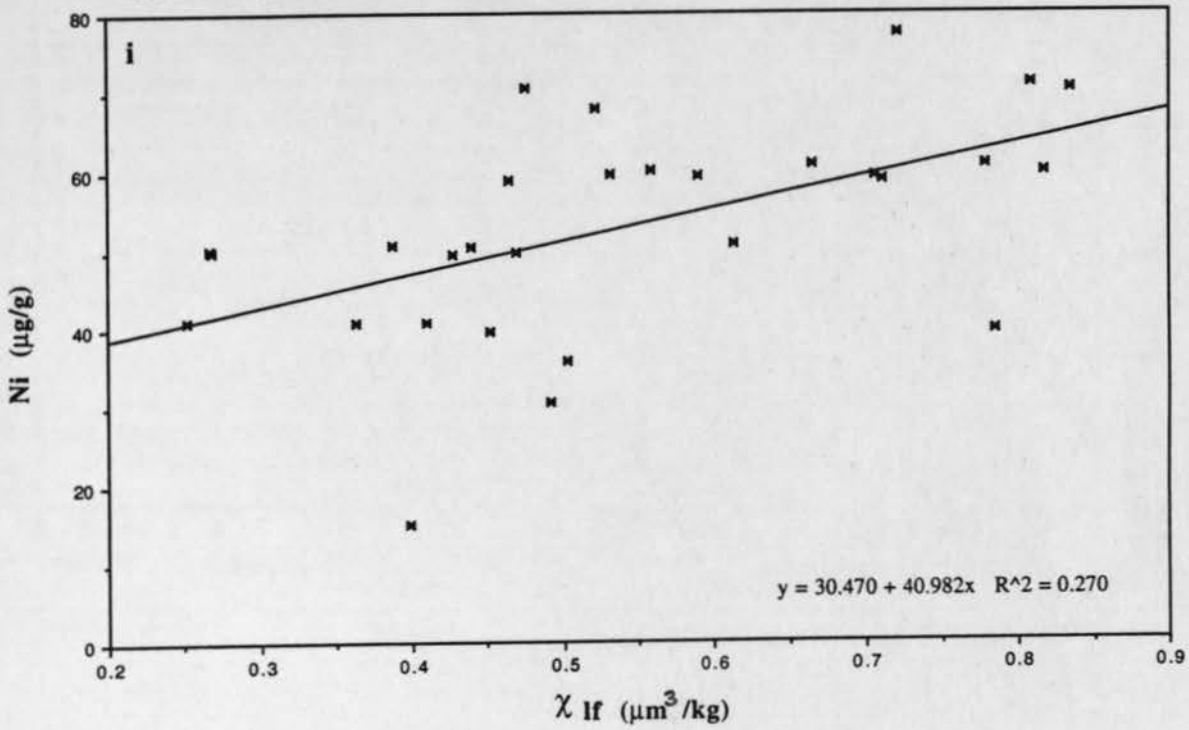


Fig 6.21 e. Regression, marsh core 1
i. Ni with χlf ii. Ni with SIRM



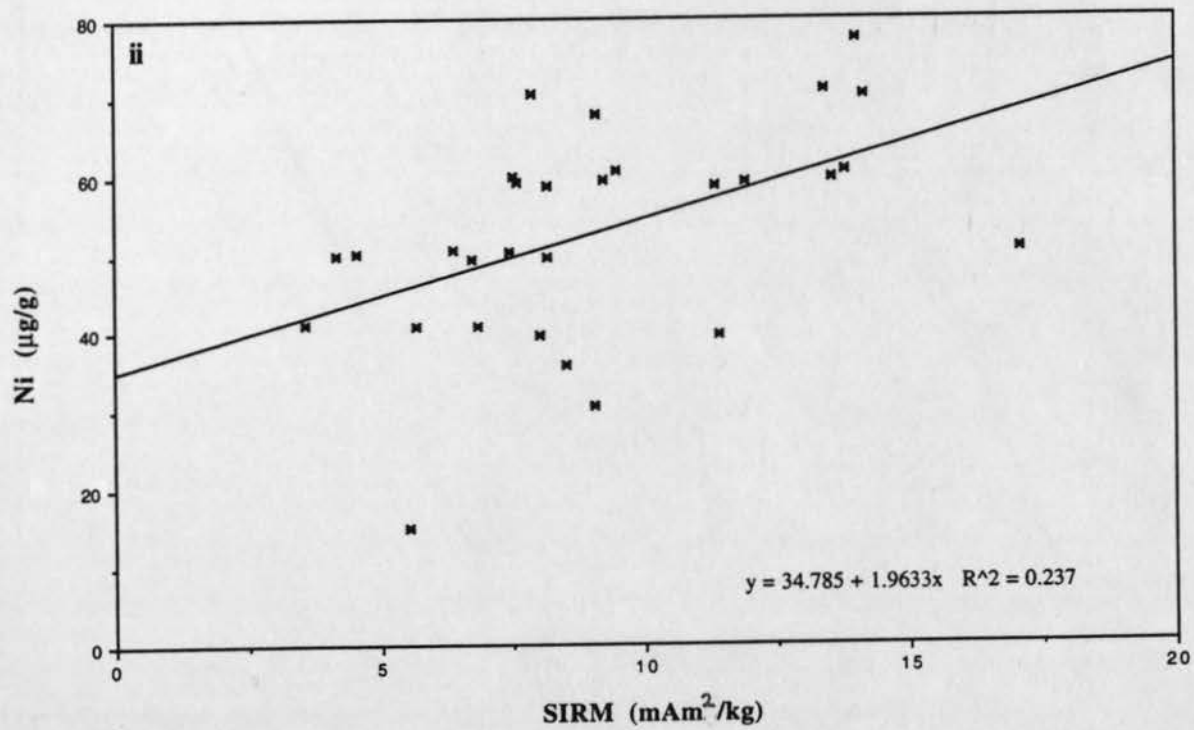
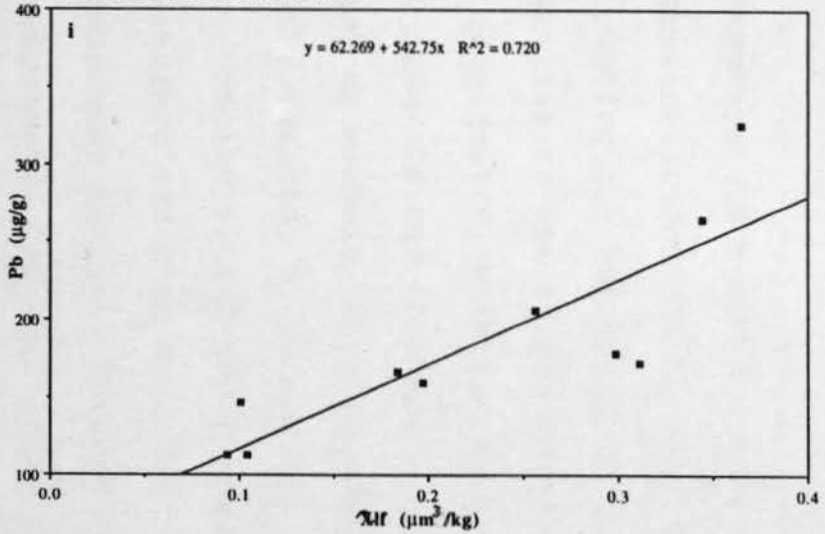


Fig 6.22 Regression, soil core A2
i. Pb with χ_{lf} ii. Pb with SIRM



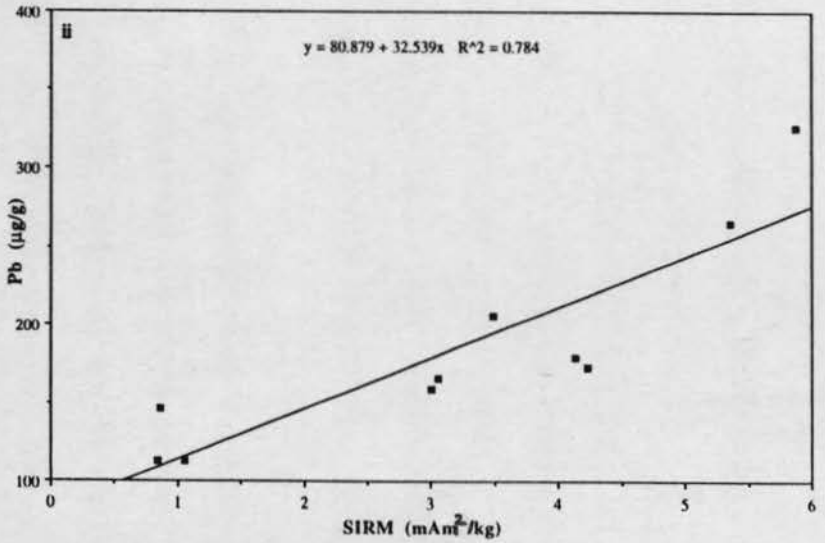
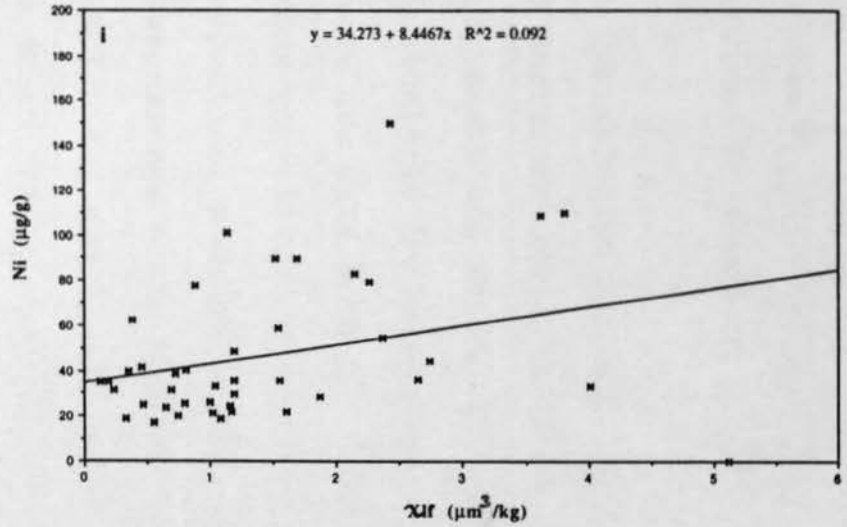
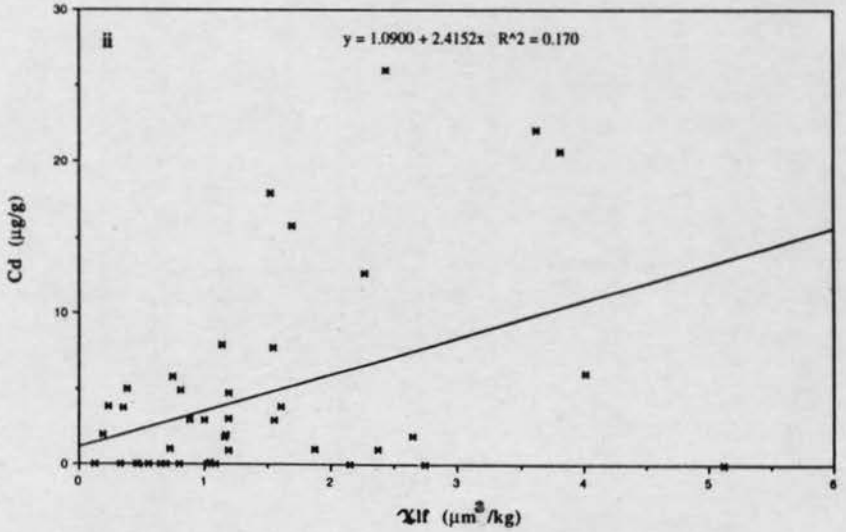


Fig 6.23 Regression, stream bed sediments
i. Ni with χ_{lf} ii. Cd with χ_{lf}





between χ_{lf} and Cd, Ni and Cu (Table 6.10 d), regression produced R^2 vales of 17.2% (Cd with χ_{lf}) and 30.5% (Ni with χ_{lf}).

Correlation between heavy metals and magnetic parameters is therefore inconsistent both between the catchment components and within the individual components. This is particularly the case when considering the marsh for which there are data both for cores and surface samples and which shows very little consistent relationship between the two properties. Regression does not indicate that mineral magnetic measurements would provide a consistent predictive tool. These conclusions are in agreement with those from both of the lakes in which little significant relationship could be demonstrated.

b. Principal Component Analysis (PCA)

Chapters 4.3 b and 5.3 b explain the reasoning behind the application of PCA to this study and its usefulness in reducing the variables in such a large set of data. PCA was applied to the 4 lake sediment cores retrieved from Wyken Pool individually, with the data from all the lake catchment components and included all the parameters common to the data set as a whole, such as heavy metals, mineral magnetic measurements, P, Fe and Mn.

Tables 6.12 a and b present the varimax rotated factor matrices and Figs 6.24 a-d plot the eigenvalues from principal component analysis between the lake cores and the catchment components. The associated percentage contribution of the

Table 6.12 Varimax rotated factor matrix
(n = 16, critical R = 0.4973 at 99%)
a. core M3
b. core M6
c. core M8
d. core M10

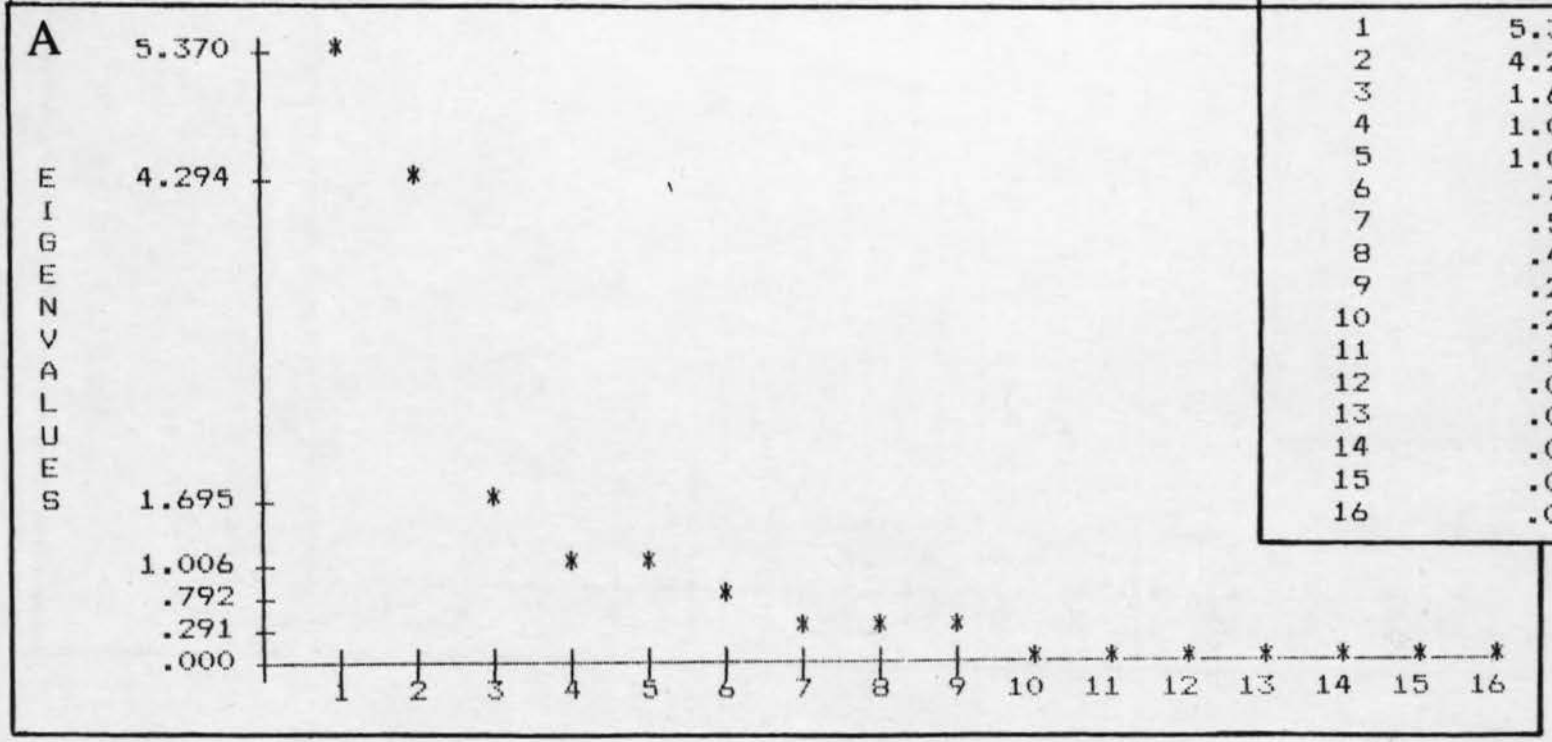
Rotated Factor Matrix:

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
A				
LFX	.06005	.93790	.27189	-.02901
HFX	.05877	.93733	.27105	-.02898
FDX	-.18540	.71676	-.05264	.18303
SIRM	-.02738	.38908	.88302	.09624
IRM	-.00223	.91515	.33235	.01162
HIRM	.00653	.29406	.86561	-.15570
S_RATIO	.08655	.17248	.15397	.67319
CD	.94235	-.03151	.02303	.02491
NI	.83257	-.00536	.12548	-.20015
PB	.91848	-.02567	.00052	.12268
CU	.81878	-.04140	.01791	.09566
ZN	.80031	-.06884	-.12455	.32148
FE	.85468	-.02453	.05157	-.18197
MN	.61989	-.02150	-.05397	.42490
FE_MN	.05477	.03117	.25590	-.81148
P	-.64868	-.13942	.13894	.35834
B				
LFX	.04846	.95397	.01687	
HFX	.04764	.95245	.01713	
FDX	-.16983	.76283	.20617	
SIRM	.00159	.78274	-.05253	
IRM	.00718	.96164	.06585	
HIRM	.03365	.69767	-.30095	
S_RATIO	.06878	.16663	.66173	
CD	.94477	-.00465	.00033	
NI	.82815	.06101	-.25042	
PB	.92331	-.00200	.09686	
CU	.81521	-.03344	.09476	
ZN	.81100	-.09256	.31857	
FE	.85054	.02486	-.22625	
MN	.62581	-.01501	.40451	
FE_MN	.09380	.17284	-.85248	
P	-.60292	-.03139	.34467	
				FACTOR 4
C				
LFX	.02438	.96047	.06177	.17177
HFX	.02340	.95886	.06066	.17169
FDX	-.18058	.78447	-.15346	.09323
SIRM	-.02037	.50622	-.00540	.76504
IRM	-.01363	.94863	-.00486	.22820
HIRM	-.00772	.33877	.23420	.86576
S_RATIO	.09497	.26186	-.59968	-.18659
CD	.94166	-.06147	.03731	.05698
NI	.80030	.02486	.33798	-.03569
PB	.91792	-.06167	-.06300	.00210
CU	.81169	-.12824	-.12778	.16359
ZN	.81635	-.14361	-.32319	.01486
FE	.82173	.03120	.36354	-.15678
MN	.64034	.05313	-.27793	-.20963
FE_MN	.01750	.10738	.87384	.03901
P	-.52463	-.33486	-.28873	.14654

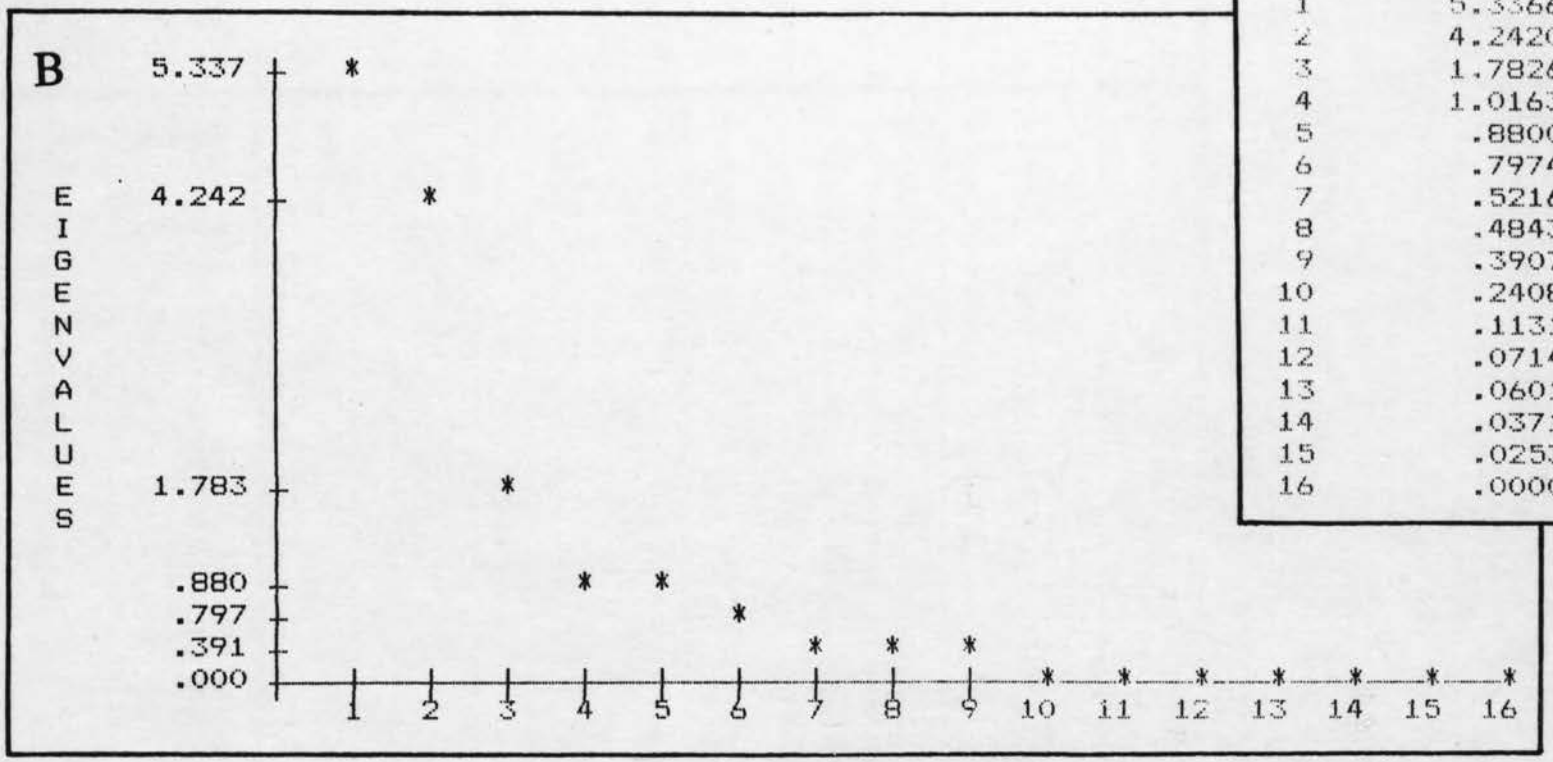
Rotated Factor Matrix:

D	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
LFX	.05448	.95632	.20341	.08863	.06046
HFX	.05596	.95573	.20214	.08949	.05808
FDX	-.27238	.74809	.06442	-.28295	.10022
SIRM	-.02961	.45776	.80532	.03680	.11617
IRM	.00334	.95385	.22918	.03572	.05986
HIRM	.00535	.29238	.90681	.07531	-.17017
S_RATIO	.07760	.25704	-.07758	-.03171	.76324
CD	.95079	-.01169	.00879	.02315	.05568
NI	.79261	-.01024	.07861	.39458	.18059
PB	.90811	-.02607	.01309	-.06552	.17272
CU	.85939	-.00407	-.00834	-.17026	-.12043
ZN	.82558	-.06050	-.06769	-.38858	.09158
FE	.78206	-.05380	.03748	.37818	.32518
MN	.54629	-.08078	.01638	-.24666	.58135
FE_MN	-.04995	.00564	.07013	.88552	-.12970
P	-.65081	-.05676	.29799	-.25935	.37273

Fig 6.24 Eigenvalues of Wyken Pool lake sediment cores and all catchment components
a. Core A0
b. Core B0
c. Core C0
d. Core D0

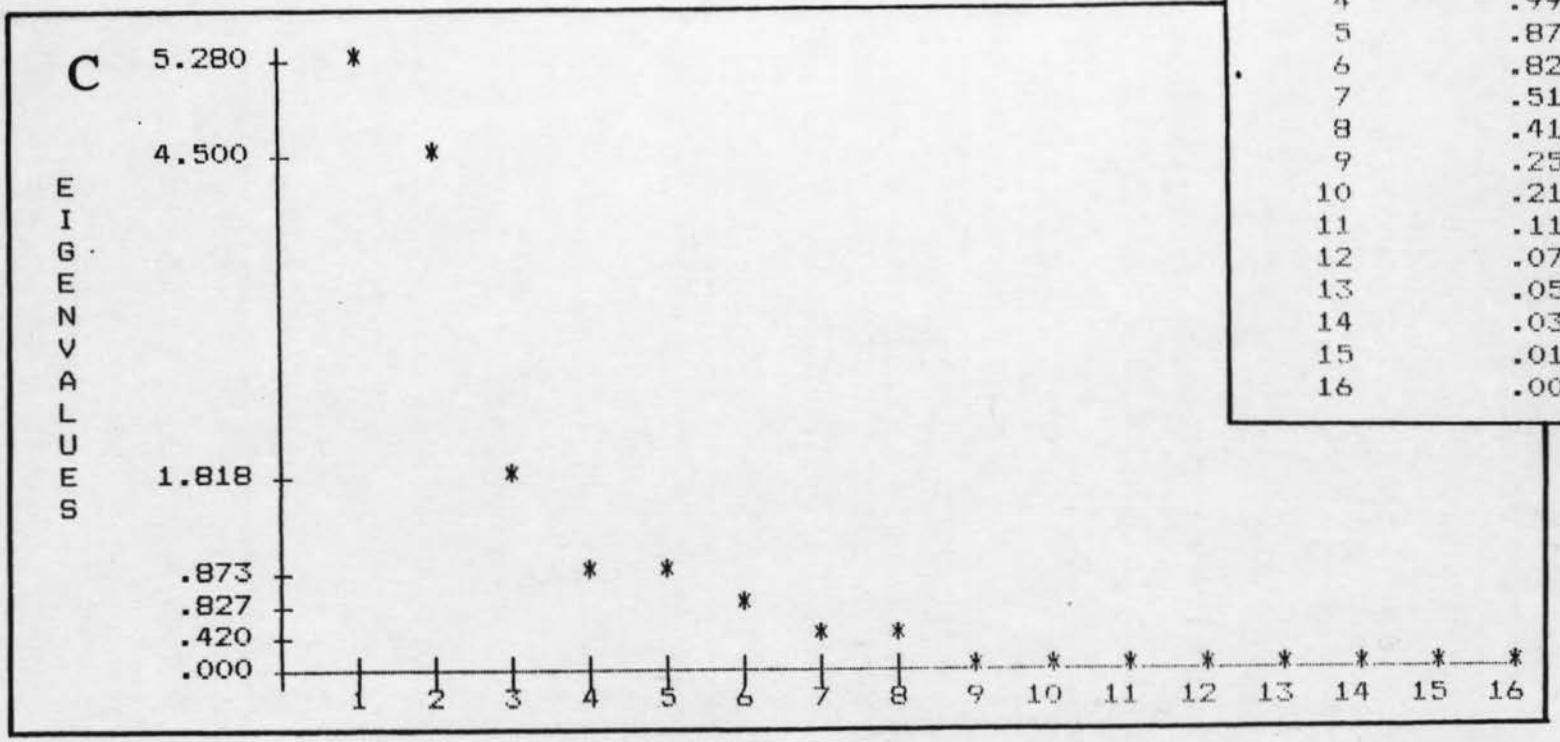


Factor	Eigenvalue	Pct of Var	Cum Pct
1	5.37028	33.6	33.6
2	4.29408	26.8	60.4
3	1.69461	10.6	71.0
4	1.06763	6.7	77.7
5	1.00636	6.3	84.0
6	.79218	5.0	88.9
7	.51967	3.2	92.2
8	.40587	2.5	94.7
9	.29143	1.8	96.5
10	.22206	1.4	97.9
11	.11544	.7	98.6
12	.09861	.6	99.2
13	.06535	.4	99.6
14	.03697	.2	99.9
15	.01942	.1	100.0
16	.00002	.0	100.0

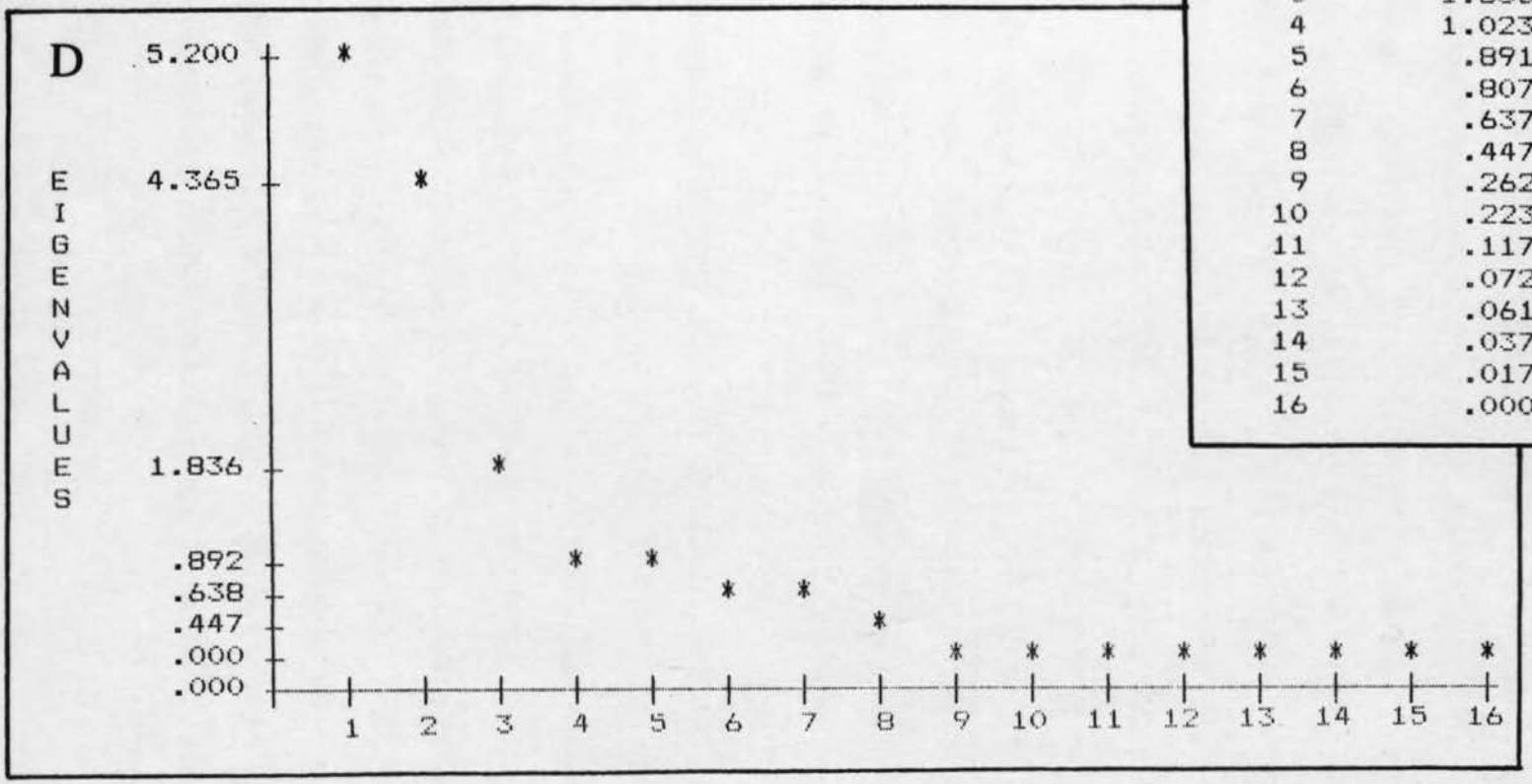


Factor	Eigenvalue	Pct of Var	Cum Pct
1	5.33661	33.4	33.4
2	4.24209	26.5	59.9
3	1.78265	11.1	71.0
4	1.01635	6.4	77.4
5	.88003	5.5	82.9
6	.79746	5.0	87.8
7	.52166	3.3	91.1
8	.48439	3.0	94.1
9	.39070	2.4	96.6
10	.24083	1.5	98.1
11	.11315	.7	98.8
12	.07145	.4	99.2
13	.06012	.4	99.6
14	.03714	.2	99.8
15	.02534	.2	100.0
16	.00006	.0	100.0

Factor	Eigenvalue	Pct of Var	Cum Pct
1	5.28002	33.0	33.0
2	4.50039	28.1	61.1
3	1.81824	11.4	72.5
4	.99855	6.2	78.7
5	.87288	5.5	84.2
6	.82654	5.2	89.4
7	.51821	3.2	92.6
8	.41978	2.6	95.2
9	.25448	1.6	96.8
10	.21672	1.4	98.2
11	.11131	.7	98.9
12	.07173	.4	99.3
13	.05903	.4	99.7
14	.03674	.2	99.9
15	.01536	.1	100.0
16	.00002	.0	100.0



Factor	Eigenvalue	Pct of Var	Cum Pct
1	5.20009	32.5	32.5
2	4.36454	27.3	59.8
3	1.83569	11.5	71.3
4	1.02355	6.4	77.6
5	.89163	5.6	83.2
6	.80701	5.0	88.3
7	.63761	4.0	92.3
8	.44748	2.8	95.0
9	.26210	1.6	96.7
10	.22316	1.4	98.1
11	.11793	.7	98.8
12	.07234	.5	99.3
13	.06136	.4	99.7
14	.03794	.2	99.9
15	.01756	.1	100.0
16	.00002	.0	100.0



factors to variance in the data set is also shown. In all four data sets, corresponding to the 4 lake cores and associated catchment component data, the first two factors contribute over 60% to the total variance. The factor matrix plots utilised factors 1 and 2 only (Figs 6.25 a-d). Table 6.13 summarises the percentage contribution of the factors with eigenvalues over 1.0 as these represent the most significant variables.

Table 6.14 summarises the dominant parameters in the first two factors. Factor 1 is mainly dominated by all the heavy metals but Fe, Mn and P also feature strongly in factor 1. Factor 2 is mainly dominated by magnetic parameters, cores AO and BO by the susceptibility-based measurements and IRM; DO as AO and BO with the addition of SIRM; and CO as DO with the addition of HIRM. PCA therefore supports evidence from correlation and regression of the lack of a relationship between heavy metals and mineral magnetic charcteristics in deposited urban sediments and soils. The two dominant factors separate into mainly heavy metals and mineral magnetic characteristics.

The factor score plots of each core with the catchment components (Figs 6.25 a - d) enable the separation of each component and an assesssment of the relationship between the various components making up the catchment of Wyken Pool. In each case, the individual components plot in approximately the same component space, this would indicate that all four cores yielded approximately the same data and therefore, in the case of Wyken Pool, the analysis of one core would have been sufficient to extrapolate along the eastern transect. All of

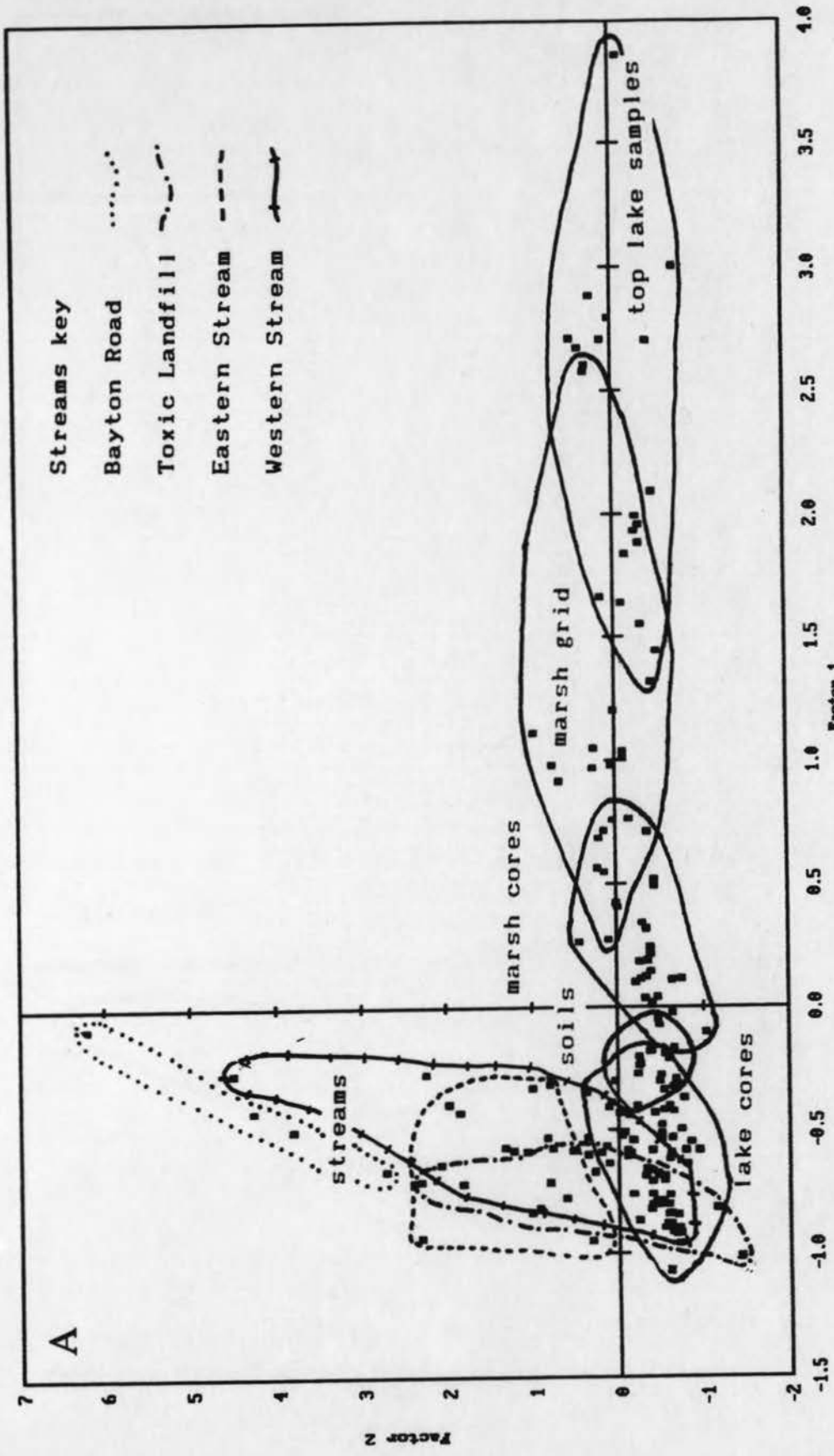
Table 6.13 Percentage explained variance of Principal Components in Wyken Pool lake cores and catchment components.

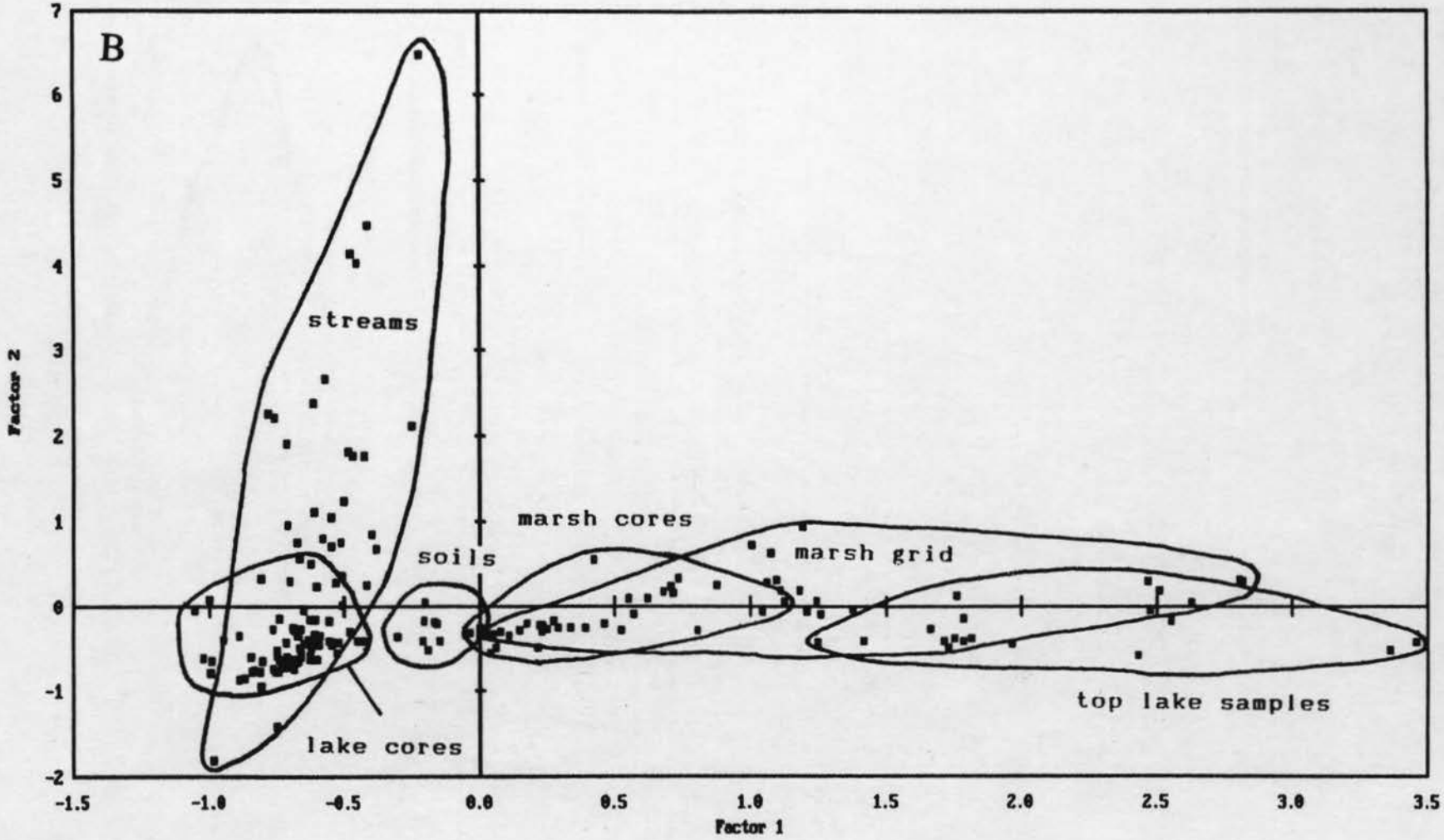
	Factor				
Core	1	2	3	4	5
AO	33.6	26.8	10.6	6.7	6.3
BO	33.4	26.5	11.1	5.5	
CO	33.0	28.1	11.4		
DO	32.5	27.3	11.5	6.4	

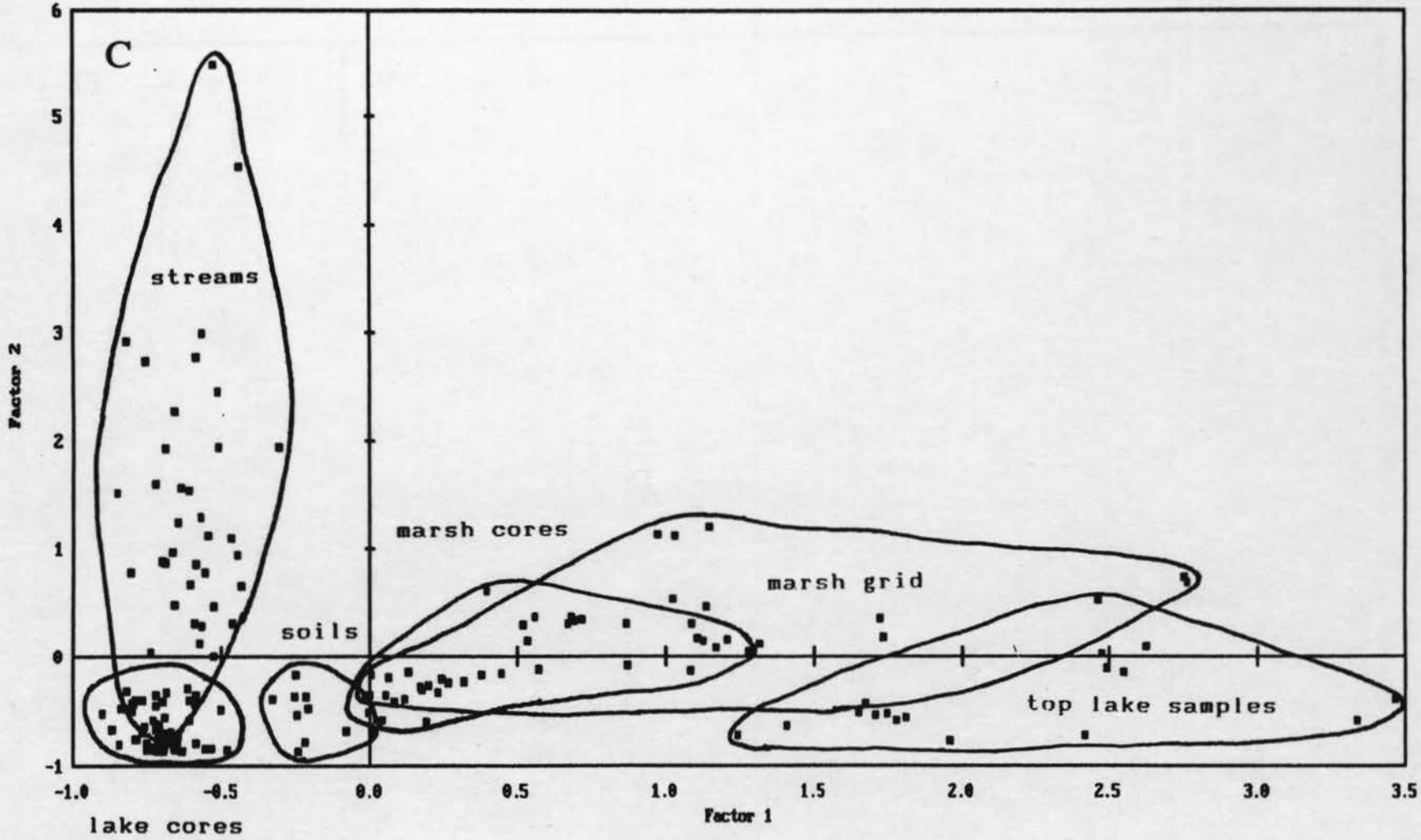
Table 6.14 Dominant parameters identified by Principal Components Analysis in components 1 and 2 in Wyken Pool lake cores and catchment components

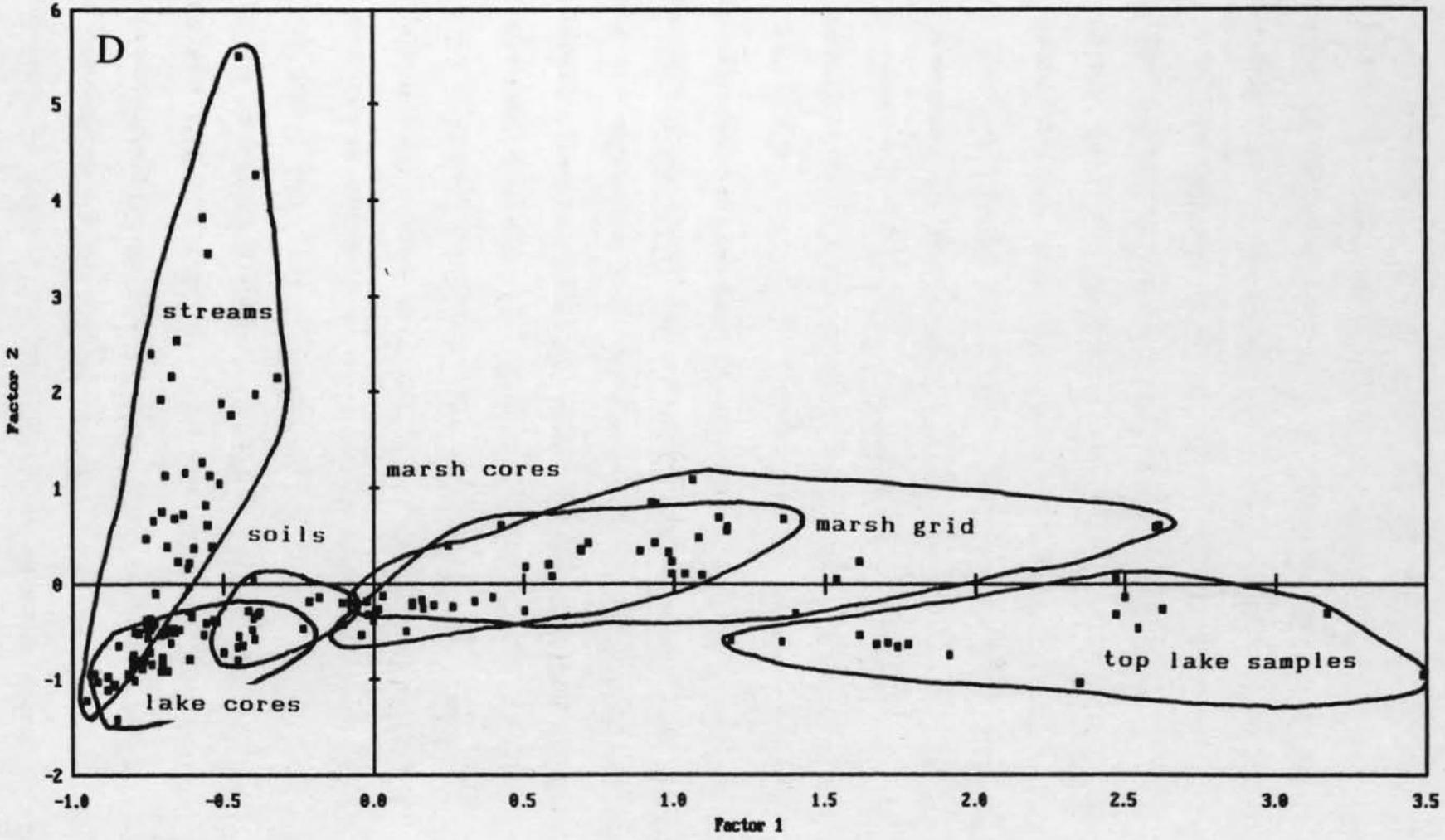
	Parameters	
	Factors	
Cores	1	2
AO	Heavy metals, Fe, Mn, P	χ_{lf}, χ_{hf}, X_{fd}, IRM
BO	Heavy metals, Fe, Mn, P	χ_{lf}, χ_{hf}, χ_{fd}, IRM
CO	Heavy metals, Fe, Mn, P	χ_{lf}, χ_{hf}, χ_{fd}, IRM
DO	Heavy metals, Fe, Mn	χ_{lf}, χ_{hf}, χ_{fd}, IRM

Fig 6.25 Principal Components Analysis of Wyken Pool lake sediment cores and all catchment components
a. Core A0
b. Core B0
c. Core C0
d. Core D0




B
streams
soils
marsh cores
marsh grid
top lake samples
lake cores
Factor 2
Factor 1
7
6
5
4
3
2
1
0
-1
-2
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5


C
streams
soils
marsh cores
marsh grid
top lake samples
lake cores
Factor 2
Factor 1
6
5
4
3
2
1
0
-1
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5


D
streams
soils
marsh cores
marsh grid
top lake samples
lake cores
Factor 2
Factor 1
6
5
4
3
2
1
0
-1
-2
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

the components except the stream samples plot along the axis representing factor 1, dominated by heavy metals, so heavy metals, and to a lesser extent Fe, Mn and P explain most of the variance in these samples. The stream samples, however, lie along the Y axis, representing factor 2 and therefore χ_{lf}, χ_{hf}, χ_{fd} and IRM explain most of the variance in these samples. The extent of overlap between the catchment components and the lake samples indicates the relationship between them. The soils tend to overlap with both the marsh cores and lake sediments at either ends of the lake, (cores AO and DO). However, in the middle two transects, there is no overlap between the lake cores and the soils. There is also considerable overlap between the lake cores and the stream samples. Fig 6.25 a (core AO) delineates the four streams making up the fluvial system at Wyken Slough. This indicates the close relationship between the lake sediments, the western stream and the drainage from the toxic landfill site, as there is considerable overlap between these three. The bed sediments from the streams draining the Bayton Road Industrial Estate are the most distinct from the lake sediments. The samples taken from the top of the marsh grid of cores overlap with those of the cores themselves indicating that the source of sediment to these two have changed little and that there is a similarity in provenance between them. However, whilst the lake cores and the top samples from the grid of lake cores both lie predominantly on the X axis, they do not overlap. Sediments deposited in the upper third of the lake cores, in particular core AO (Fig 5.6), are less dense with higher concentrations of heavy metals than the middle third of the

core. The divergence of the top samples from the bulk of the lake core may therefore indicate the effect of an influx of denser, less contaminated sediment during the building of the Longford housing estates, Bayton Road Industrial Estate, the M6 motorway and the improvement of drainage through the marsh in the 1950s, 60s and 70s which is discussed in Chapter 5.2.3.

PCA therefore addresses the question of the relationship between the catchment components and the sediment in the lakes. It also reinforces the lack of a significant and consistent relationship between heavy metals and mineral magnetic characteristics as the two dominant factors are clearly divided between mineral magnetic characteristics and heavy metal concentrations. These findings fly in the face of those of Revitt *et al.* (1981), Hunt *et al.* (1984), Beckwith *et al.* (1986 and 1990) and Brilhante *et al.* (1989) who found a good correlation between the magnetic signal and heavy metals. This is discussed further in Chapter 8.4.

6.7 Water Quality in Wyken Pool

Chapter 2.8 v discussed the analysis of water quality in Wyken Slough in terms of four main questions:

- What are the prevailing environmental conditions at the site?

- How stable are the sinks of heavy metals likely to be under the prevailing environmental conditions?

- Do the data have a seasonal pattern?

- Do salt concentrations reach a level which may result in remobilisation of heavy metals?

Three sets of data were collected in order to address the above questions. A water quality survey was carried out in January 1988 and April 1990; secondary water quality data was obtained from the NRA (Severn Trent Region) and regular testing of water samples taken at monthly intervals from the five stations shown on Fig 2.10 b.

The monthly data were compared with average water quality data from the NRA (Severn Trent Region) of local rivers (Table 4.23), data in Bottrill (1994) for rivers in Warwickshire (Table 4.24), and Prescribed Concentrations or Values (PCVs) for potable water (Table 4.24). PCVs are stringent standards laid down by the Water Supply (Water Quality) Regulations, 1989 and enforced by the Drinking Water Inspectorate (Severn Trent Water, 1994) and provide ideal values against which those from Wyken Slough may be compared.

This section is divided into three subsections which address the four questions outlined above.

a. Prevailing environmental conditions

i. In situ analysis

Water quality characteristics measured during the first survey on 16 January 1988 are presented in Table 6.15. The

measurements were taken from a boat, at the three depths indicated on Table 6.15 and at the stations indicated on Fig 2.10 b as W1 and W2.

Table 6.15 Water quality characteristics of Wyken Pool.

Site	Depth m	pH	O mg l^{-1}	O % sat	Temp °C	Eh mv
W1	0	8.0	10.9	84.6	4.2	27
W1	0.3	8.1	10.7	82.9	4.4	84
W1	0.6	7.9	7.2	56.3	4.6	-31
W2	0	8.2	11.0	84.6	4.2	27
W2	0.4	8.2	10.4	80.0	4.1	30
W2	0.8	8.2	9.9	76.2	4.2	32

W= Wyken Pool

Locations on Fig 2.10 b.

From this survey, it was found that Wyken Pool was alkaline, with an average pH of 8.1 at both sampling sites. Dissolved oxygen levels above the mud-water interface exceeded 80% saturation and there was no evidence that the lake is stagnant or deoxygenated. Lower values at the mud-water interface represent still water trapped in benthic weed leading to partially deoxygenated conditions. The pH remained

fairly constant with depth at both sampling stations, but Eh at site W1 decreased markedly with depth in contrast to site W2 perhaps indicating localised anoxic areas in the lake.

The second survey was carried out in April 1990 at five sites (WS1 - WS5, Fig 2.10 b) which included measurements of the inflowing streams and the outflow as well as the lake water. The chemical characteristics of the two inlets at Wyken Pool (Table 6.16) reflect the differences between their contributing catchments. The Wyken Slough Brook, site WS2 (Fig 2.10 b for location) has a high conductivity reflected in the highest concentrations recorded for all except NO_2, PO_4 and Si. In contrast, the eastern inflow, WS1, (Fig 2.10 b) has a much lower concentration of all elements including the major pollutants. The lake water chemistry at Wyken Pool generally reflects the dominance of the inflow from site WS2. Between the inflow and the outflow there is some reduction in the concentrations of Cl, Na and K and a reduction in conductance to under 1000 $\mu S\ cm^{-2}$. Pollution is therefore reduced by storage and uptake in the body of the lake. Water quality downstream is still generally poor in comparison with rural rivers, but of average quality for urban streams (Thoms, 1987).

The PCV is exceeded by K, NH_4 and NO_2 concentrations although WS1, the eastern stream, is consistently below all PCVs and WS5, the outlet, does not exceed the NH_4 PCV. All other concentrations and values are less than the appropriate PCV. Comparing the data from Wyken Pool with those of other Warwickshire rivers, summarised in Table 4.23 (Bottrill,

Table 6.16 Chemical analysis of water samples from Wyken Pool. Based on one survey carried out in April 1990

Sample[1]	WS1	WS2	WS3	WS4	WS5
pH	7.7	7.9	8.1	8.1	7.8
Conductivity[2]	816	1288	1020	1025	981
Ca[3]	60.0	83.4	70.5	73.0	71.4
Mg[3]	35.2	56.8	47.2	39.2	43.5
Na[3]	30.1	49.3	40.9	38.8	33.2
K[3]	7.2	16.0	12.8	12.8	12.3
NH_4	0.09	1.8	0.82	0.94	0.4
NO_3	3.02	11.05	8.15	10.36	8.29
NO_2	0.02	0.35	0.44	0.29	0.18
SO_4	23.9	39.9	31.1	30.5	27.4
HCO_3	297.8	393.0	346.6	285.7	324.6
Cl	48.41	89.61	70.29	65.46	63.04
PO_4	0.01	0.04	0.08	0.11	0.1
Si	6.75	6.45	6.86	6.78	6.75

[1] Location of sampling points on Figure 2.10 b
[2] $\mu s\ cm^{-1}$
[3] $mg\ l^{-1}$

1994), NO_2 still appears high, but all other parameters are comparable with the ranges given in Table 4.24.

ii. NRA (Severn Trent Region) water quality data

Figs 6.26 a - c show general water quality characteristics and Table 6.17 summarises the mean heavy metals data for four sites on the Wyken Slough Brook, from the NRA (Severn Trent Region) during various periods extending from 1974 - 1987 (see site details for Figs 6.26 a - c). Appendix 3 contains documents from STWA explaining the data and enlarging on tipping practise at the Hawksbury landfill site. The data indicate a number of pollution incidents over the variable length of record available as shown by the maximum concentrations of several pollutants. Site 1, the drainage from Hawksbury tip downstream of the water purification plant, appears to make a major contribution to the low oxygen and high salinity levels recorded in the Wyken Slough Brook and in Wyken Pool itself. It is also a site with extremely high Biological Oxygen Demand (BOD), ammoniacal nitrogen (NH_4-N) and oxidised nitrogen (TON). Water quality at the other sites is typical of urban streams (Thoms, 1987). The data show high maxima in some of the parameters indicating the number and severity of the events occurring throughout the catchment. Zn and Cu (Table 6.17) have highest concentrations at site 1, whereas peak concentrations of Ni, Pb and Cd are to be found variously at sites 2, 3 and 4 on the main stream of the Wyken Slough Brook. These high values suggest significant enhancement from either urban storm drainage or the metal

Site details for Figures 6.26 a - d

Site 1 = Hawksbury Tip downstream of effluent treatment plant
1974 - 1987

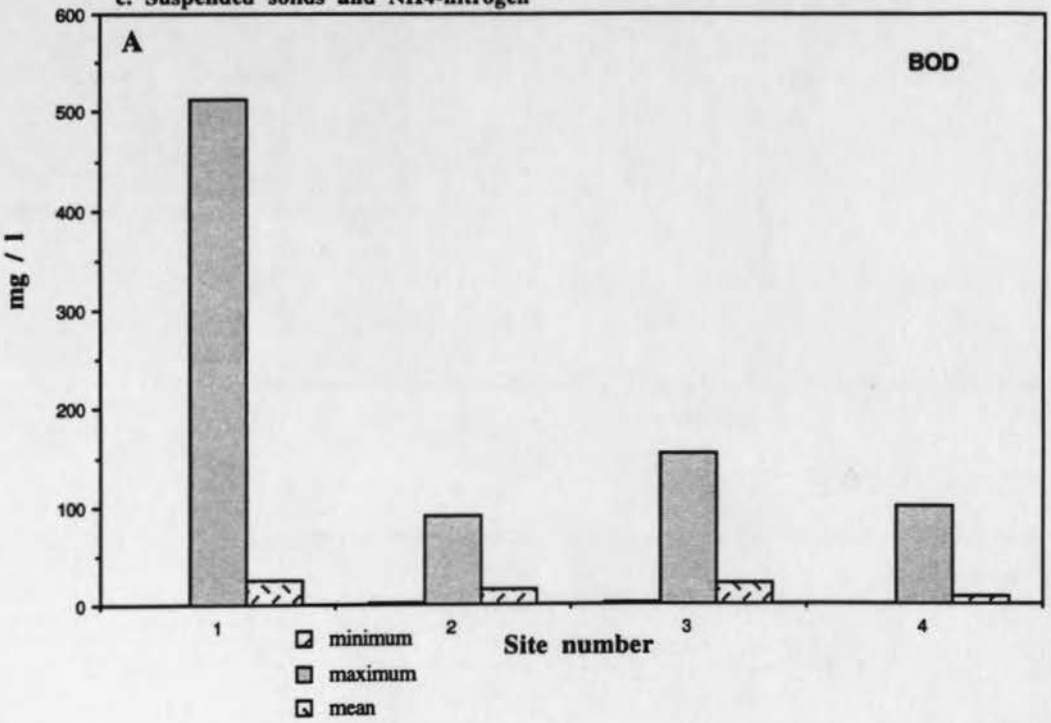
Site 2 = Wyken Slough Brook downstream of the Bayton Road Industrial Estate
1977 - 1982

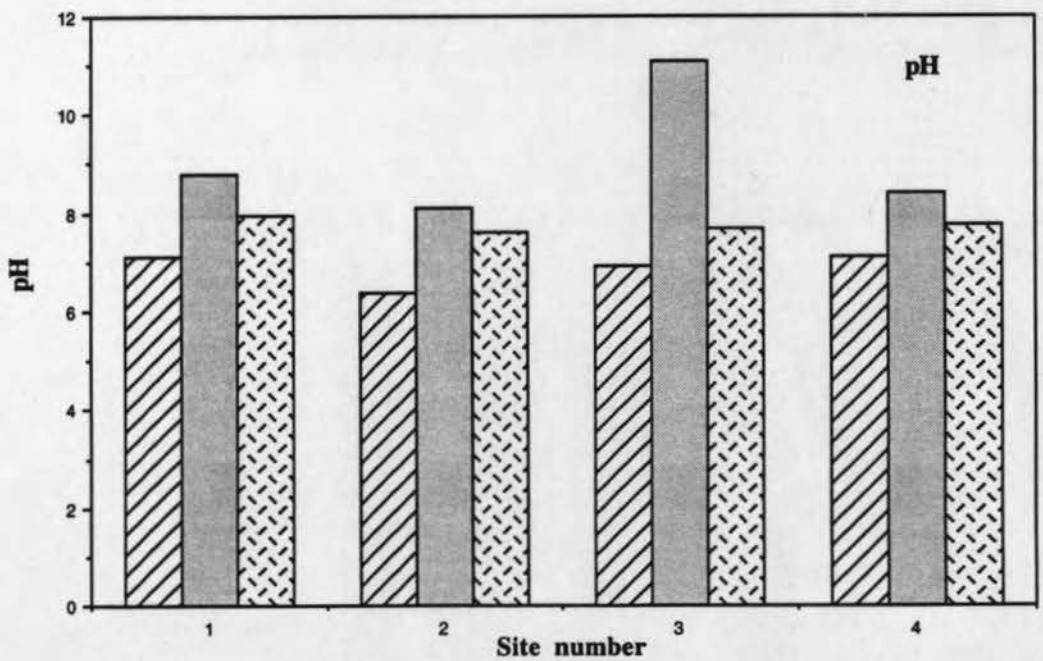
Site 3 = Wyken Slough Brook rear of factory on the Bayton Road Industrial Estate
1978 - 1987

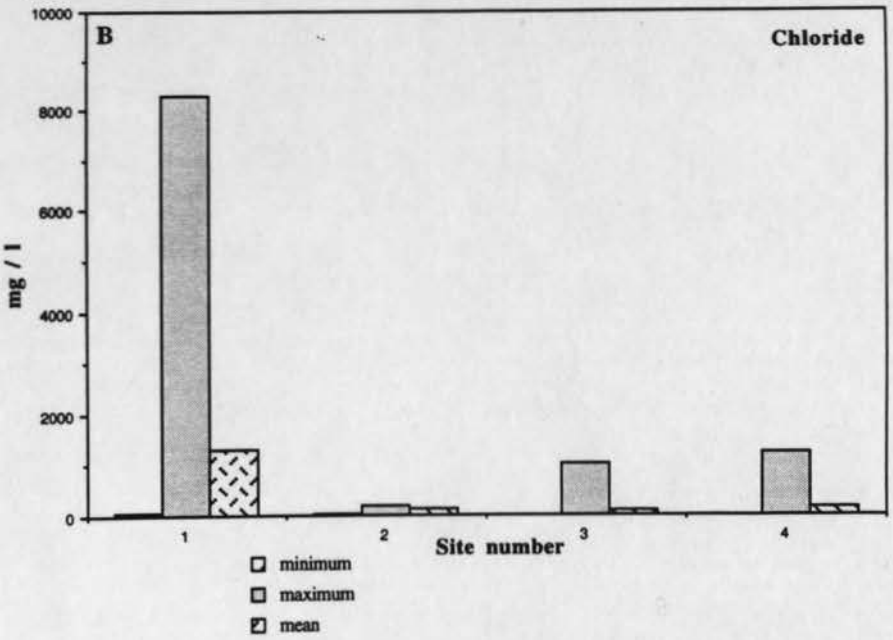
Site 4 = Wyken Slough Brook inflow to Wyken Pool
1984 - 1987

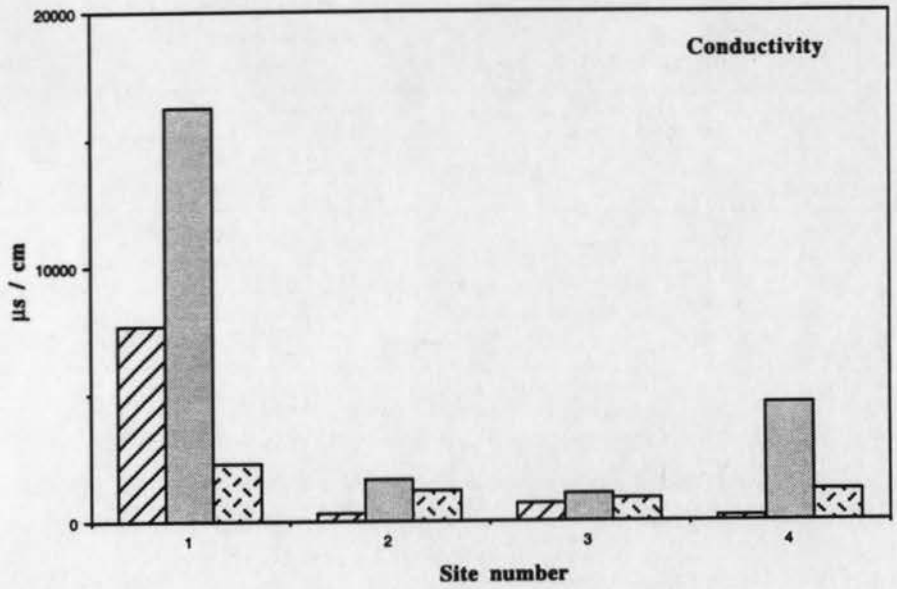
Locations of above sampling sites on Fig 2.10 b

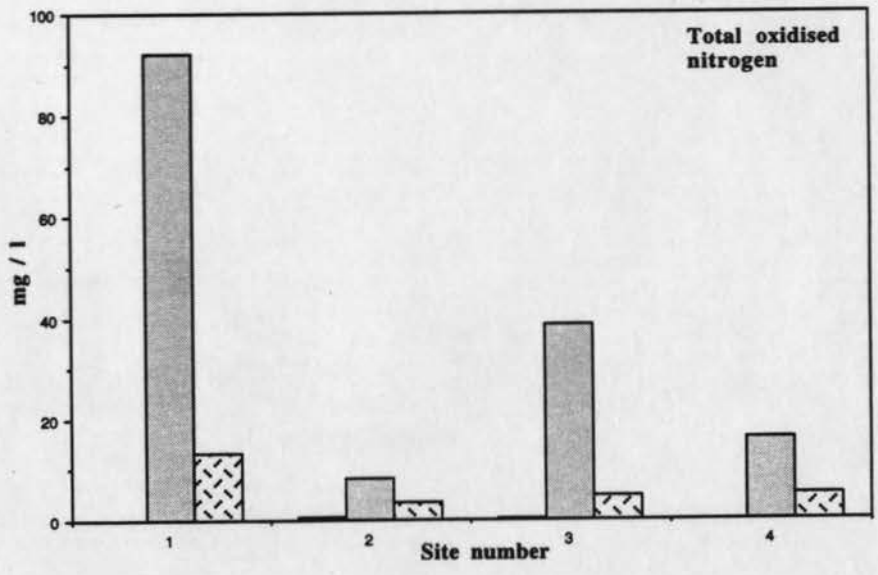
Fig 6.26 NRA (Severn Trent region) water quality data for 4 locations in the Wyken Slough catchment
a. BOD and pH b. Chloride, conductivity and total oxidised notrogen (TON)
c. Suspended solids and NH4-nitrogen

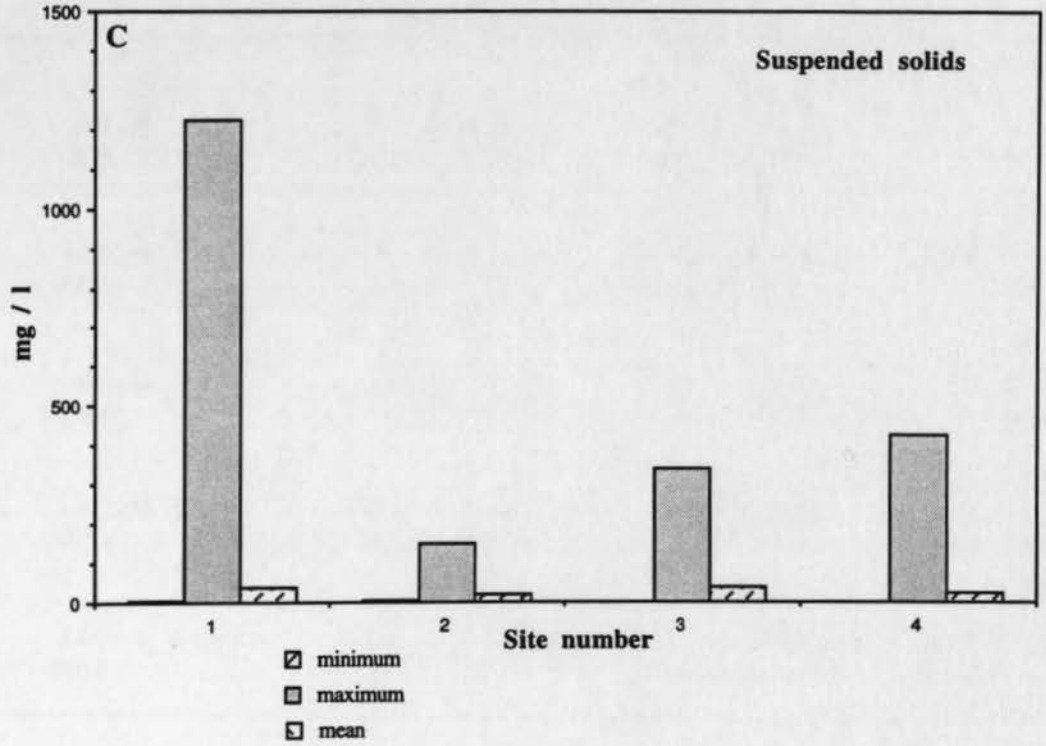





B
Chloride
10000
8000
6000
4000
2000
0
mg / l
1
2
3
4
Site number
minimum
maximum
mean


Conductivity
20000
10000
0
µs / cm
1
2
3
4
Site number


Total oxidised nitrogen
100
80
60
40
20
0
mg / l
1
2
3
4
Site number


C
Suspended solids
1500
1000
500
0
mg / l
1
2
3
4
Site number
minimum
maximum
mean

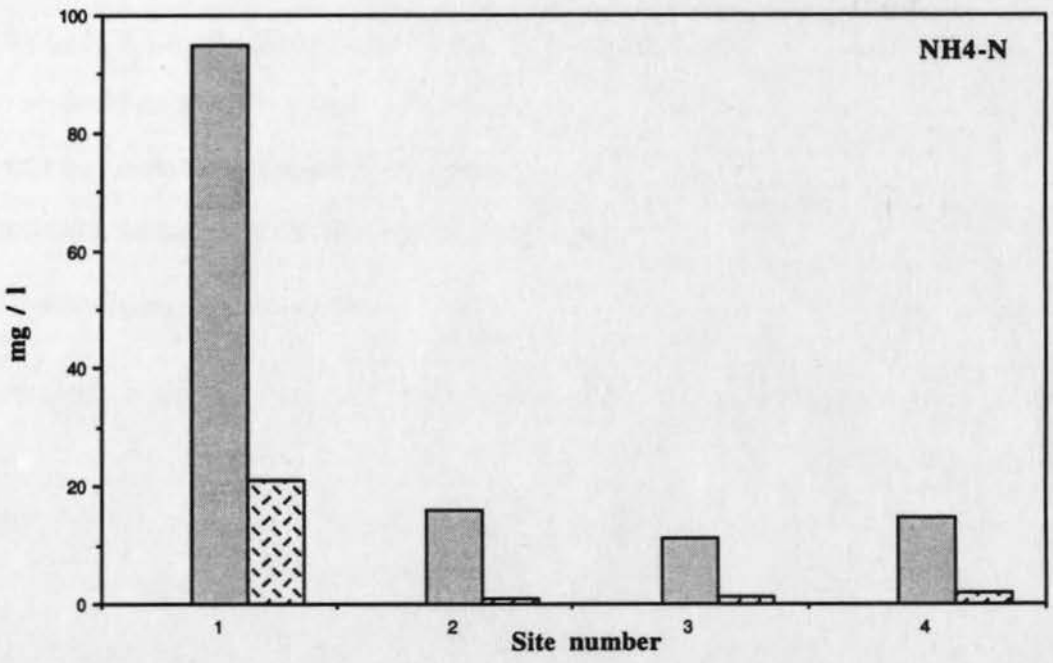

NH4-N
100
80
60
40
20
0
mg / l
1
2
3
4
Site number

Table 6.17 Summary NRA (Severn Trent Region) mean heavy metals concentrations from Wyken Slough Brook ($\mu g\ l^{-1}$).

Site	1	2	3	4
Cd				
T	15.0 (46)	10.0 (52)	33.0 (82)	6.0 (68)
F	NDA	10.0 (27)	10.0 (28)	5.6 (55)
Cu				
T	320.0 (48)	70.0 (52)	220.0 (82)	177.5 (69)
F	NDA	70.0 (27)	160.0 (28)	99.0 (55)
Pb				
T	40.0 (46)	20.0 (52)	60.0 (82)	25.2 (68)
F	NDA	20.0 (27)	20.0 (28)	16.5 (55)
Ni				
T	60.0 (49)	40.0 (52)	40.0 (82)	42.0 (67)
F	NDA	50.0 (27)	20.0 (28)	45.0 (55)
Zn				
T	880.0 (49)	110.0 (52)	890.0 (82)	265.0 (68)
F	NDA	100.0 (27)	34.0 (28)	144.0 (54)

1 = Hawksbury tip downstream of the effluent treatment plant

2 = Wyken Slough Brook downstream of Bayton Road Industrial Estate

3 = Wyken Slough Brook rear of factory on Bayton Road Industrial Estate

4 = Wyken Slough Brook inflow to Wyken Pool

(52) = indicates number of samples

T = total metal concentration

F = metal concentration in filtrate

NDA = no data available

plating and other industrial activities on the Bayton Road Industrial Estate.

Over the period 1974-1987, the western inflow to Wyken Pool exhibited high BOD, NH_4-N and total oxidised nitrogen and, on occasions, might be expected to bring about at least partial deoxygenation of the entire lake body.

Table 6.18 presents PCVs for heavy metals in potable water and average heavy metal concentrations in river waters from NRA (Severn Trent Region). Only in the case of Ni in the Class 3 River Sowe at Stoneleigh is the PCV exceeded. However, in the case of the Wyken Slough Brook, the PCV is exceeded in Cd (all sites), Pb (site 3) and Ni (sites 1 and 2). Wyken Slough Brook would therefore seem to be of poor quality in comparison with the water chemistry of other rivers in Warwickshire.

b. Seasonality of water quality in Wyken Pool

Table 6.19 summarises the variations in concentrations obtained for water in Wyken Pool and its inlets and outlet. Locations of the sampling sites are shown on Fig 2.7b. Maximum values for some non-metallic elements exceed the PCV (Mg, K and Na) as do NO_2 and NH_4, but no heavy metals appear in concentrations higher than the appropriate PCV.

Temperature (Fig 6.27 a) reflects the seasonal cycle with a maximum of 19.5° C recorded at site WS2 in July and a minimum of 2° C recorded at site WS4 in November. Temperatures began to rise in February and declined after July. To various degrees, this seasonality is reflected in the other results obtained. There is a fluctuation in pH between a high of 8.7 at site WS4

Table 6.18 Prescribed Concentrations and Values (PCVs) for heavy metals in potable water compared with heavy metal concentrations in river water in Warwickshire ($\mu g\ l^{-1}$).

	1	2	3	4	5	6
Cd						
T	0.3	0.4	2.1	0.1	0.27	5.0
F	0.2	0.2	1.4	0.1	0.3	
	n=12	n=23T	n=24T	n=1	n=13	
		n=21F	n=22F			
Cu						
T	9.0	12.0	36.0	3.0	8.7	3.0
F	9.0	8.7	20.0	3.0	7.3	
	n=12	n=23T	n=24T	n=1	n=13T	
		n=22F	n=22F		n=11F	
Pb						
T	3.0	11.3	9.3	2.0	3.7	0.05
F	1.0	1.0	1.7	1.0	1.0	
	n=12	n=23T	n=24T	n=1	n=13T	
		n=21F	n=22F		n=11F	
Ni						
T	15.7	11.0	83.7	3.0	3.0	0.05
F	13.7	9.7	74.3	3.0	4.0	
	n=12	n=23T	n=24T	n=1	n=13T	
		n=21F	n=22F		n=11F	
Zn						
T	37.7	42.3	139.0	36.0	22.3	5
F	31.0	27.0	110.7	22.0	22.3	
	n=12	n=22T	n=24T	n=1	n=13T	
		n=20F	n=22F		n=11F	

1 = River Avon at Tewkesbury (grid ref SO 893 332)
2 = River Sowe at Baginton (grid ref SP 338 752)
3 = River Sowe at Stoneleigh (grid ref SP 332 728)
4 = Finham Brook at Finham Bridge (grid ref SP 331 740)
5 = River Leam at Leamington (grid ref SP 308 654)
6 = PCV water quality standards

n= number of samples, a single figure represents the number of samples analysed for both filtered and total heavy metal concentration
T= Total
F= Filtered

From Severn Trent Water Authority, 1988/1989 (1 - 5) and 1994 (6).

Table 6.19 Maximum and minimum values for water quality in Wyken Pool

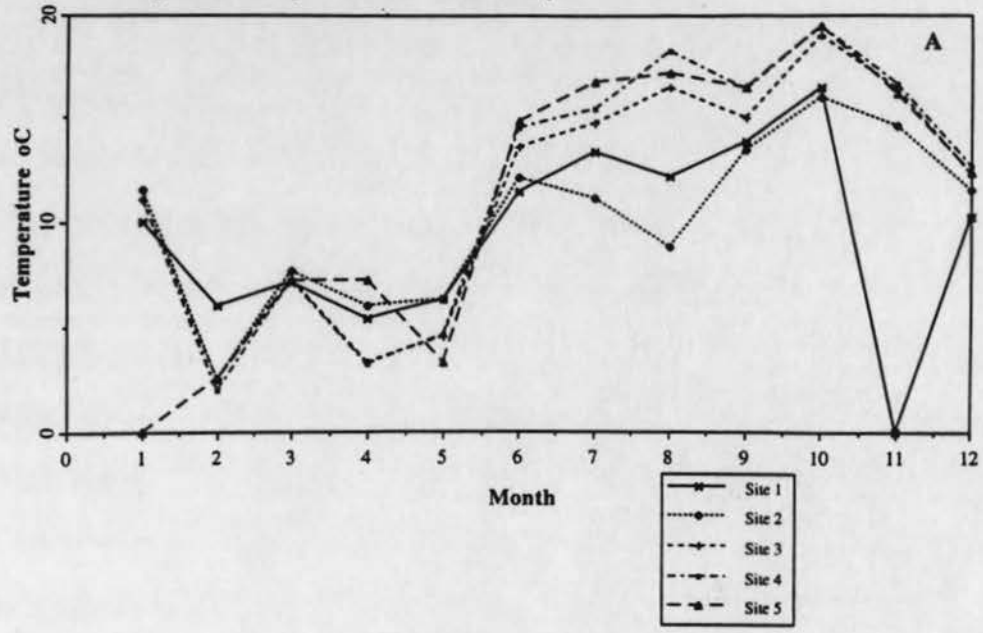
Variable	Minimum	Maximum
Mg^{2}	8.4	63.0
Ca^{2}	27.5	119.0
K^{2}	4.2	25.0
Na^{2}	16.5	294.0
Cd^{1}	0.0	3.5
Cu^{1}	0.0	18.0
Ni^{1}	0.0	9.0
Zn^{1}	0.0	32.0
Pb^{1}	0.0	130.0
NO_3^{2}	0.09	15.9
NO_2^{2}	0.0	4.2
Si^{2}	0.04	0.7
PO_4^{2}	0.0	1.3
NH_4^{2}	0.0	4.0
SO_4^{2}	34.6	207.7
Cl^{2}	11.5	68.8
°C	2.0	19.5
pH	5.73	8.7
TC	312.0	2750.0

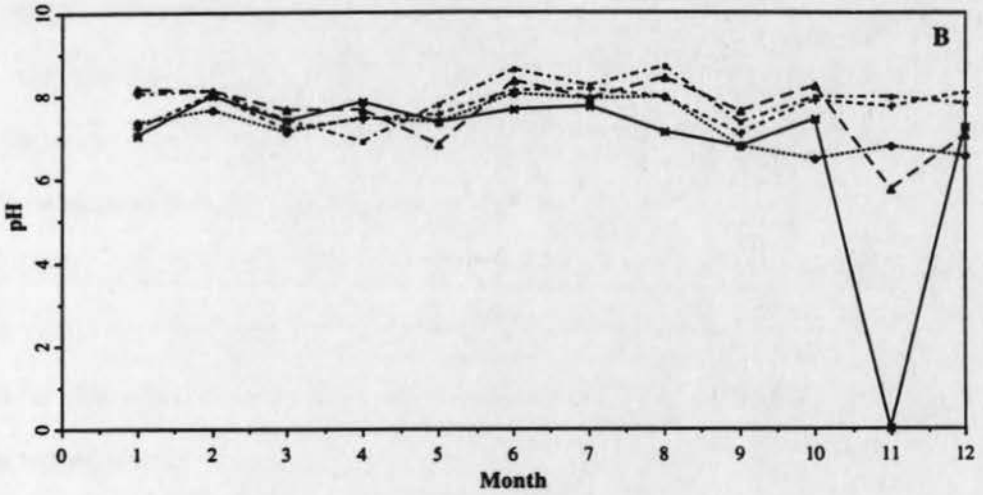
element concentrations in $^{1}\mu g\ l^{-1}$, $^{2}\ mg\ l^{-1}$

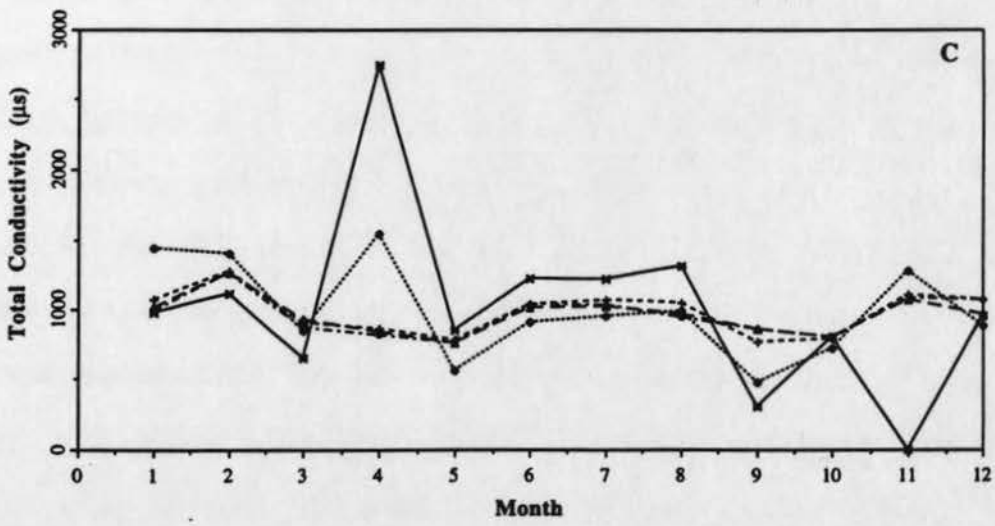
TC = conductivity measured in $\mu S\ cm^{-3}$

°C = temperature

Fig 6.27 Monthly water quality monitoring, Wyken Pool
a. Temperature b. pH c. Total conductivity





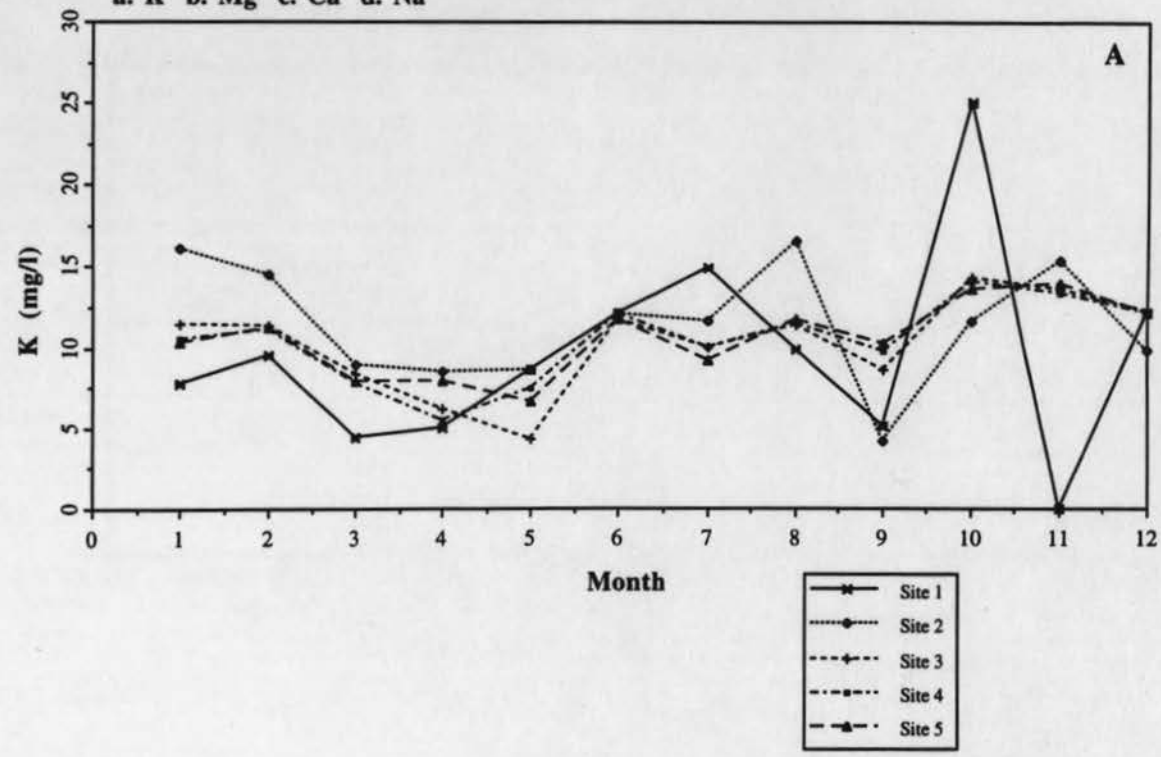


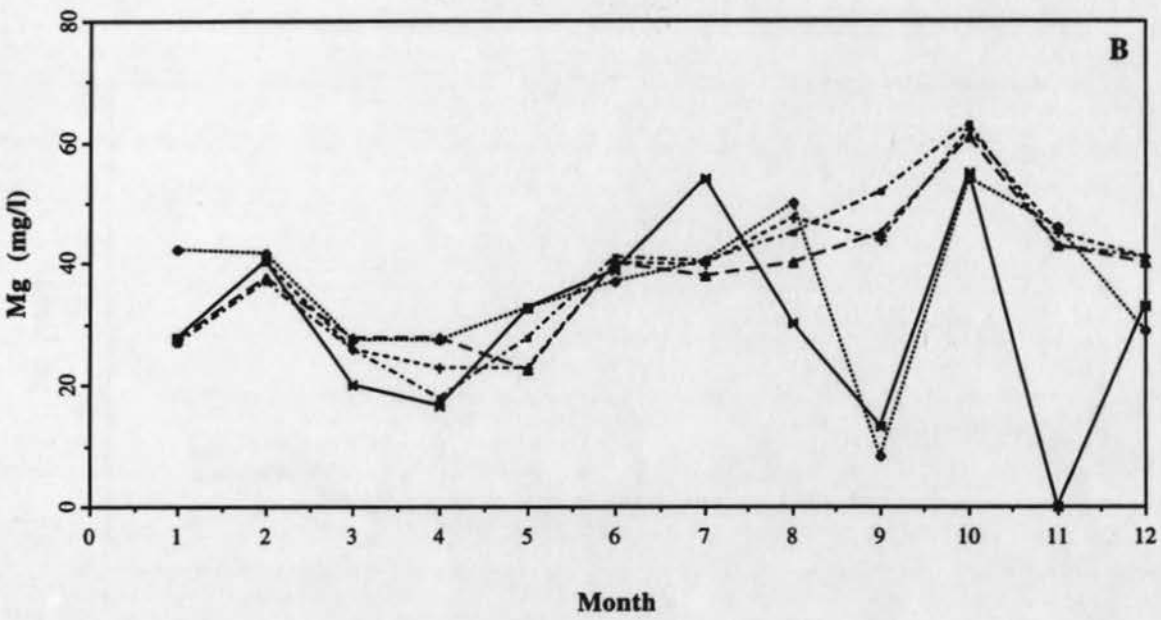
in May and a low of 5.7 at site WS5 in August. The trend is for higher pH values (Fig 6.27 b) during the spring and lower pH values in the summer and autumn months. In general, the inlets display the lowest pH values, with sites WS4 and WS5, the southern end of the lake and the outlet, exhibiting generally higher pH overall. Site WS3, situated nearest the western stream inlet, is mainly intermediate between these two sites. As discussed in Chapter 2.5 iii, low pH promotes competition between H^+ and metal ions for binding sites and leads to the release of metals from the sediments into the overlying water column. Values for pH as low as 5.7 may indicate an environment approaching acidity levels for metals to begin to be remobilised (see Fig 2.8). This was, however, only found at one site (the outflow) and occurred only once. All other pH measurements were above 6.

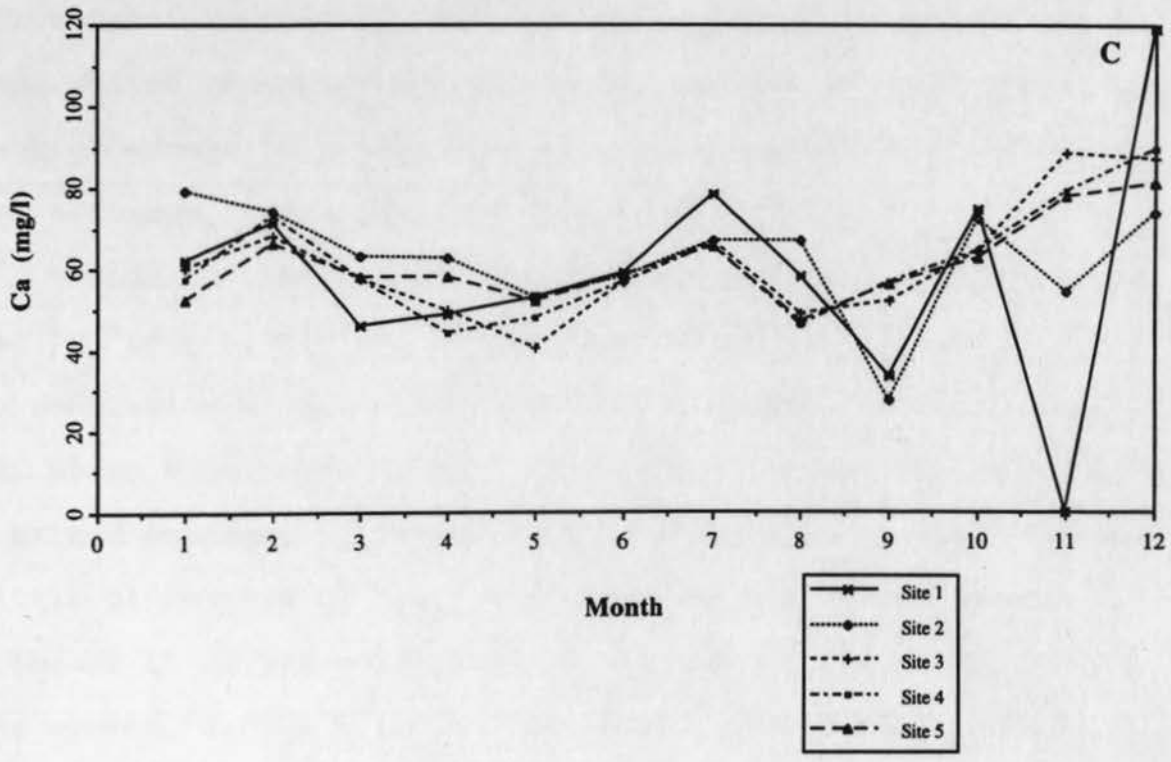
Conductivity (Fig 6.27 c) varies between a high of 2750 $\mu S\ cm^{-2}$ at site WS1 in the month of January to a low of 300 $\mu S\ cm^{-2}$ also at site WS1 during June. The inlets at sites WS1 and WS2 show the greatest variability during the year especially in January and June. The other sites vary between 700 and 1350 μS during February and November repectively. The gross seasonal fluctuations are also seen at sites WS3, WS4 and WS5 with generally higher conductivities in the autumn and lower values in the winter and early summer months.

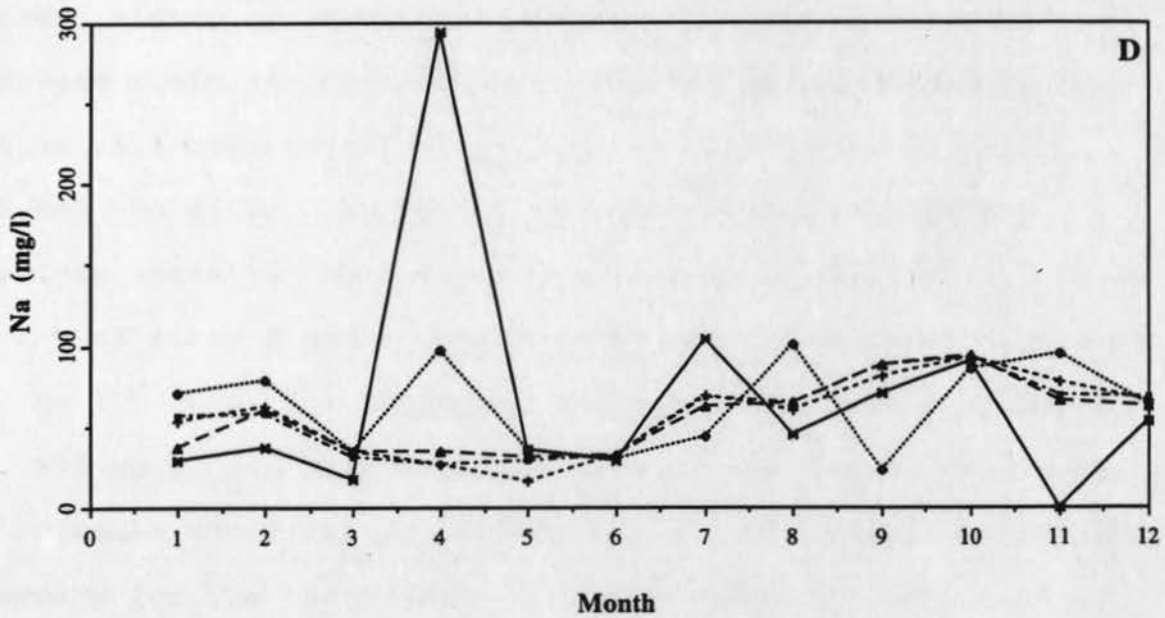
Trends in K, Mg (Fig 6.28 a and b), Ca and to a certain extent Na (Figs 6.28 c and d) parallel one another with concentrations decreasing during the winter, rising during the early spring, and being lower again in the early summer followed by a rise during mid summer. There are peaks in Na

Fig 6.28 Wyken Pool monthly water quality monitoring, non-metallic elements a. K b. Mg c. Ca d. Na






C
Ca (mg/l)
0
20
40
60
80
100
120
0
1
2
3
4
5
6
7
8
9
10
11
12
Month
Site 1
Site 2
Site 3
Site 4
Site 5

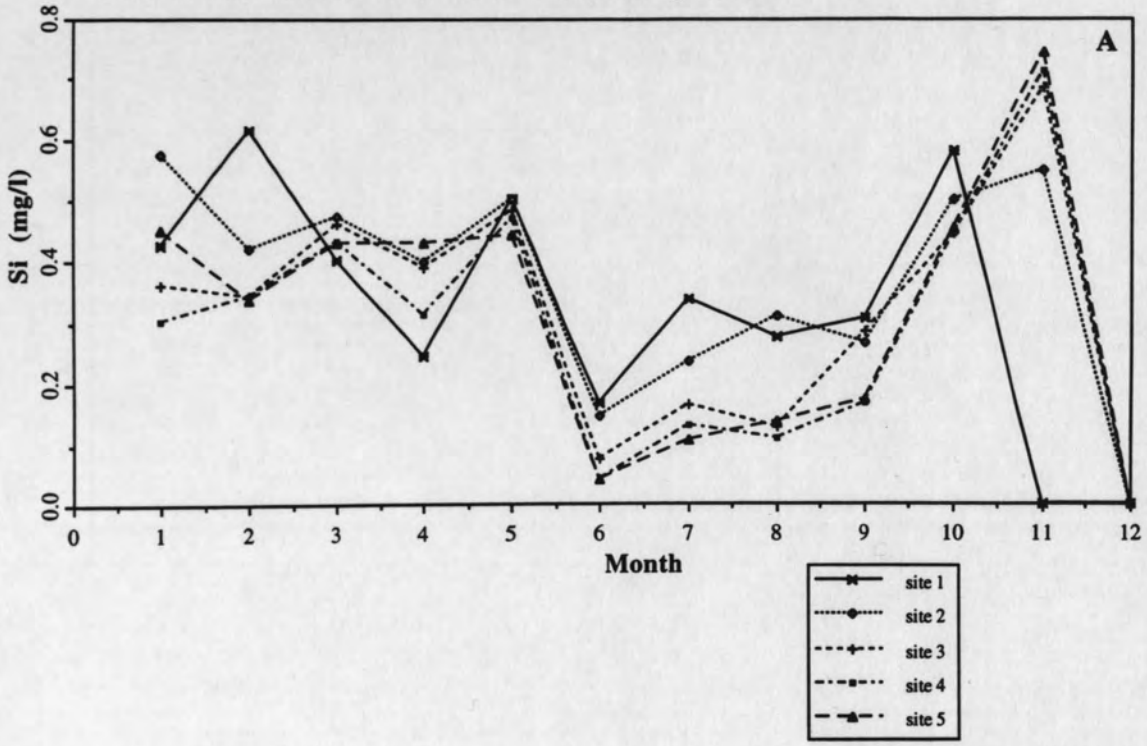

D
Na (mg/l)
0
100
200
300
0
1
2
3
4
5
6
7
8
9
10
11
12
Month

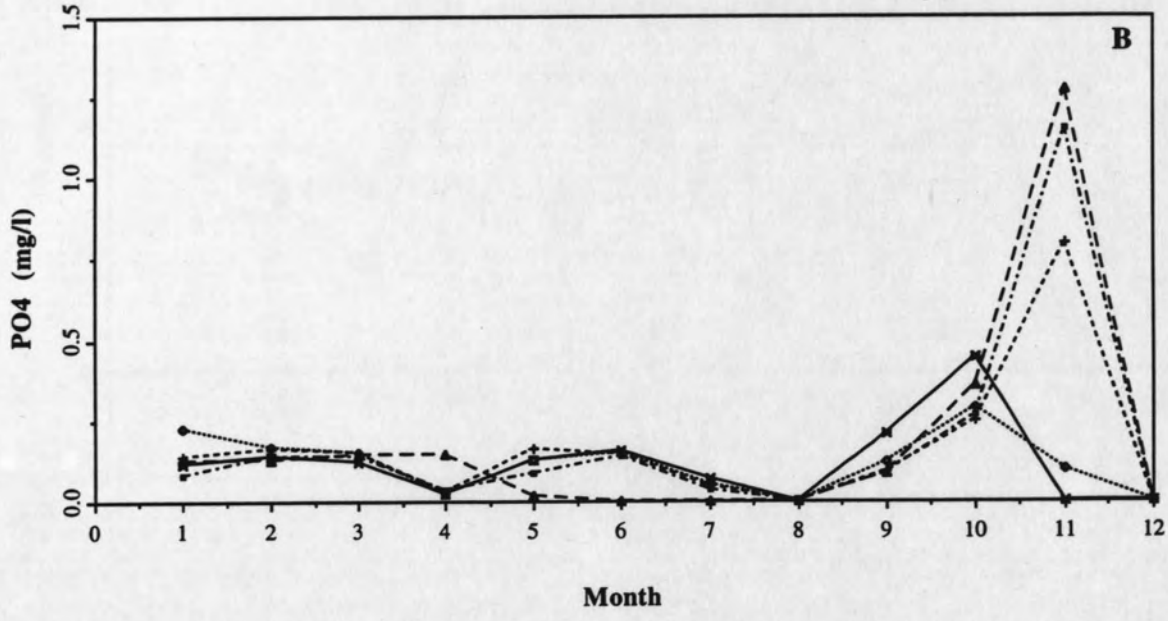
concentration in both inlets during January, at 294 mg l^{-1} and 100 mg l^{-1} for sites WS1 and WS2 respectively. These higher concentrations probably reflect the application of road salt and, whilst occassionally exceeding the PCV, do not appear to be high enough to promote heavy metal remobilistion (Förstner and Wittmann, 1981; Förstner and Kersten, 1988).

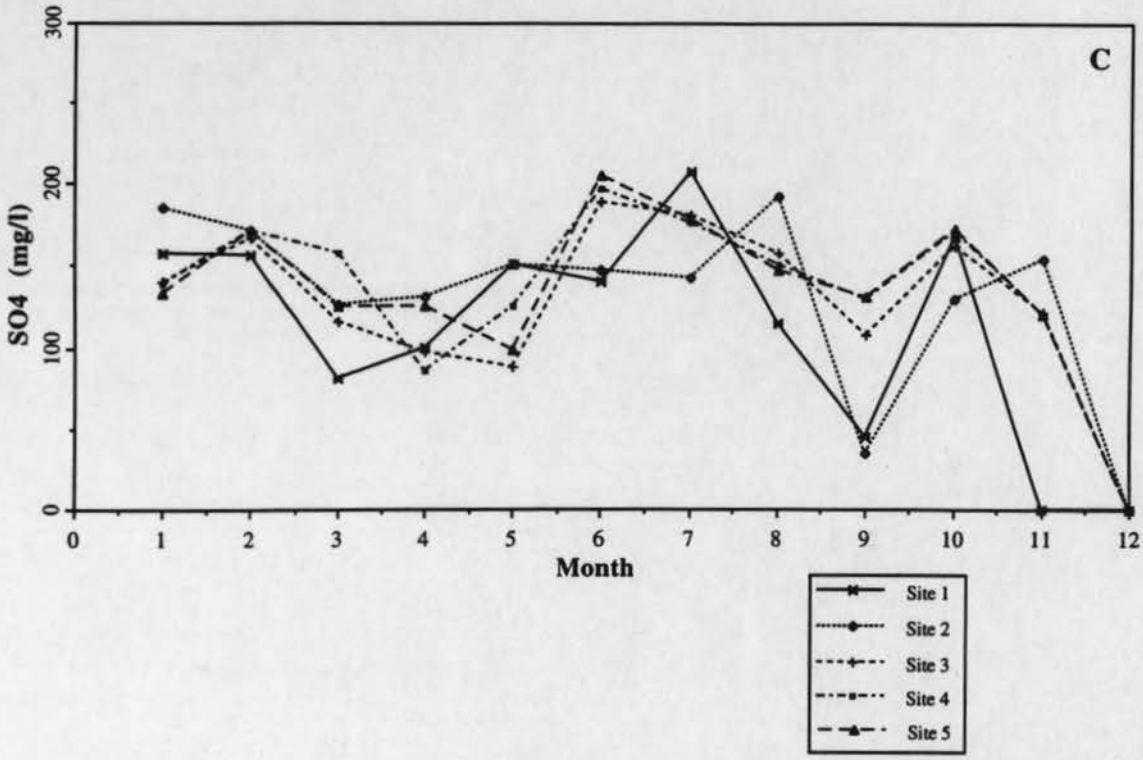
Trends for the anions indicate seasonality in that both Si and PO_4 (Fig 6.29 a and b) show marked increases in concentration at all sites during the summer, although site WS2 shows a decrease in both elements in August. There is also a marked decrease in levels in the early spring. There is very little difference in the trends between individual sites although it is the outflow which has the lowest values during the spring. Variability in the concentrations of Si and PO_4 may reflect algal blooms in the spring and summer.

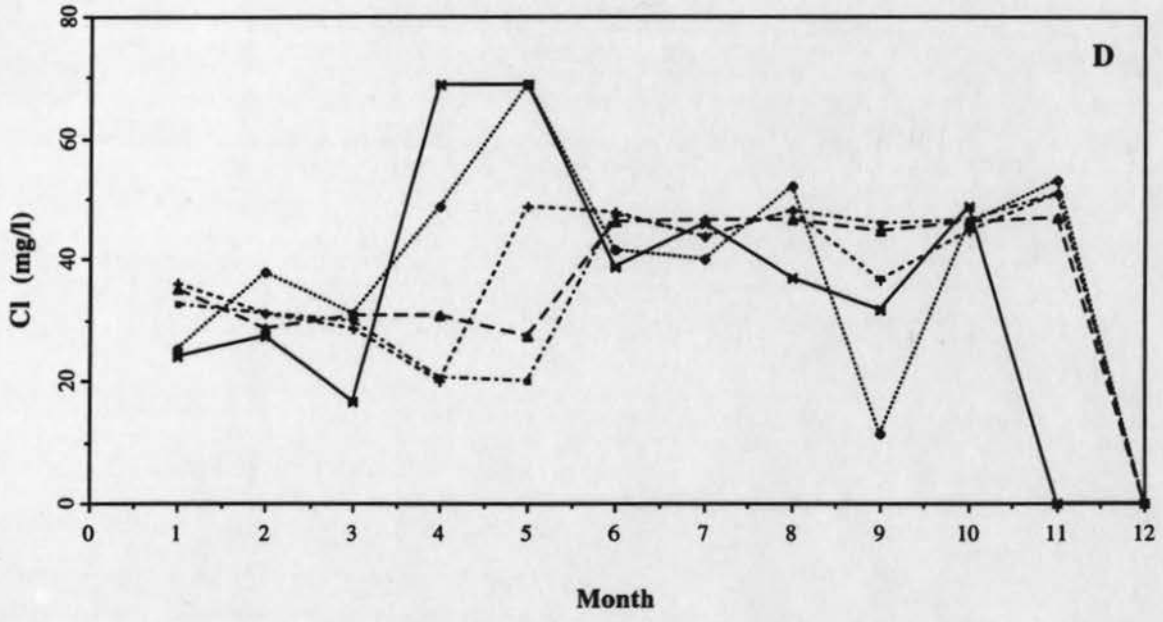
In general, SO_4 levels (Fig 6.29 c) decrease in the winter, slowly increase during the early spring and then decrease again in July before slowly increasing again in the autumn. Although there is not a great deal of difference between the sites, the values for the inlets exhibit the greatest variation with the lowest values in July of 40 and 50 mg l^{-1} at sites 2 and 1 respectively and the highest values of 210 mg l^{-1} at site 1 in April, 205 mg l^{-1} at site 5 in March and 195 mg l^{-1} at site 2 during May. Trends for Cl (Fig 6.29 d) resemble those for SO_4 except for a peak during January and February for the two inlets. NO_2 concentrations (Fig 6.29 e) are generally below 1 mg l^{-1}, except in the spring when values reach a maximum of over 4 mg l^{-1} in the outlet, the eastern inlet shows no increase, remaining at less than 0.5 mg l^{-1}.

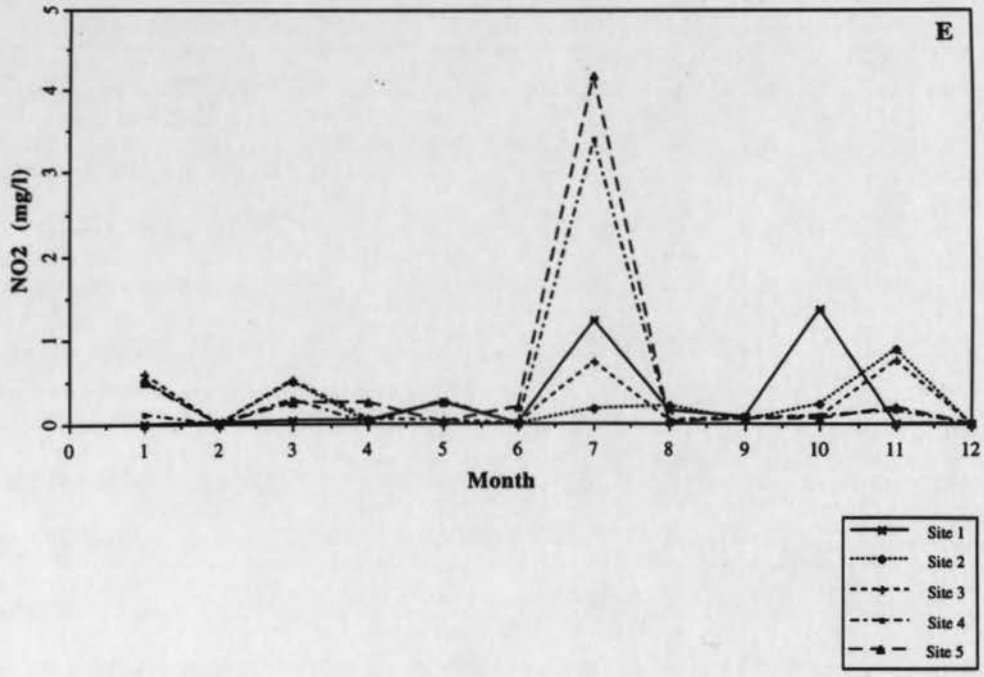
Fig 6.29 Wyken Pool monthly water quality monitoring
a. Si b. PO4 c. SO4 d. Cl e. NO2 f. NO3 g. NH4

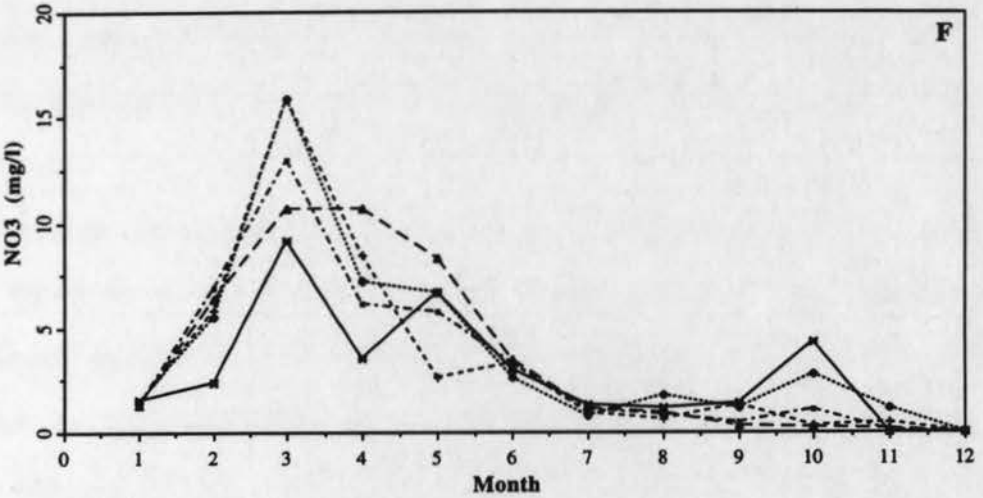


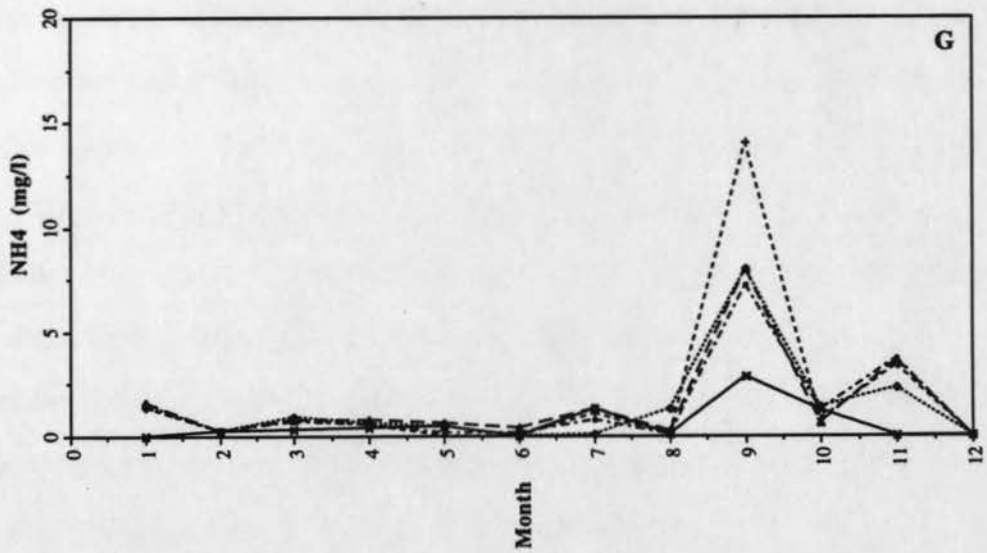



C
SO4 (mg/l)
300
200
100
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Month
Site 1
Site 2
Site 3
Site 4
Site 5


D
Cl (mg/l)
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Month


E
NO2 (mg/l)
Month
Site 1
Site 2
Site 3
Site 4
Site 5


F
NO3 (mg/l)
Month

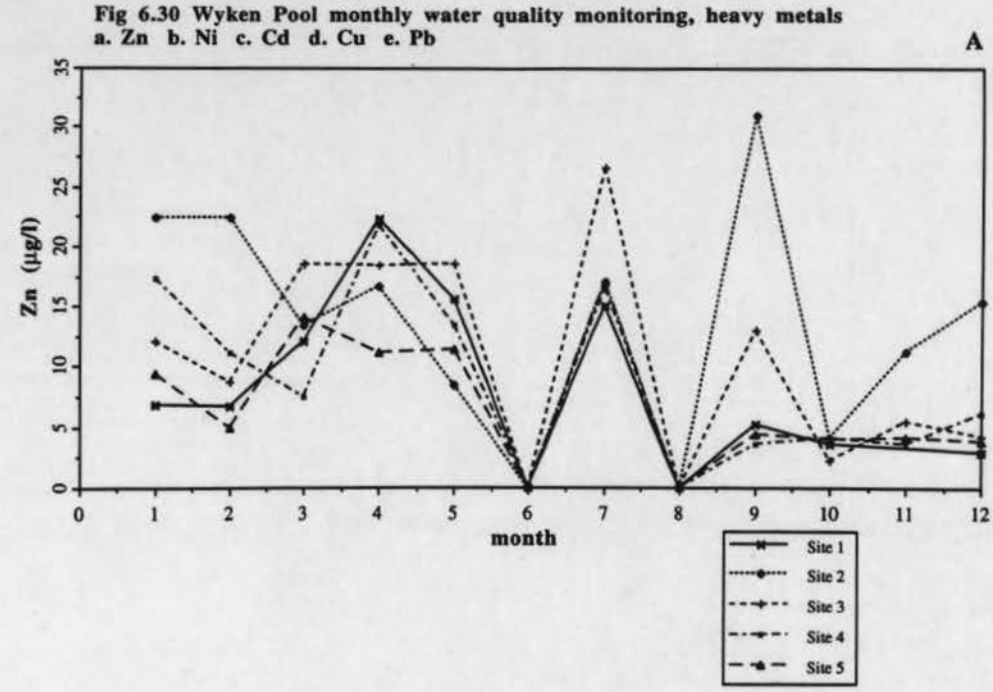

G
NH4 (mg/l)
Month

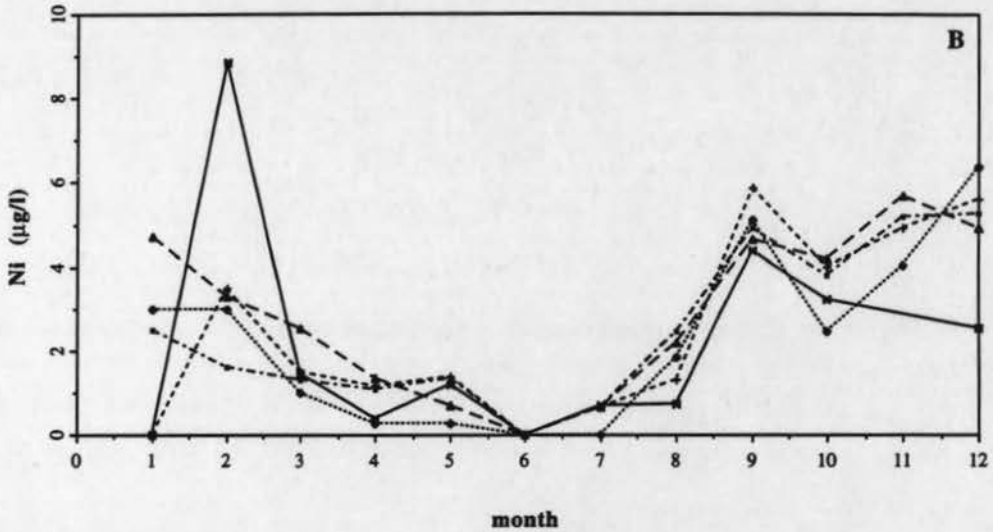
NO_3 concentration (Fig 6.29 f) is highest in the autumn at over 16 mg l^{-1} at sites WS2 and WS3. The lowest value is for the western inlet of over 9 mg l^{-1}. Values for NO_3 decline during the spring and summer, reaching a low for all sites sampled of less than 2 mg l^{-1} in September. Highest values for NH_4 (Fig 6.29 g) occur in the summer months, particularly associated with the western stream and the northern end of the lake. Lowest levels are associated with the outlet and the southern part of the lake and could be the effect of dilution of incoming stream water in the main body of the lake.

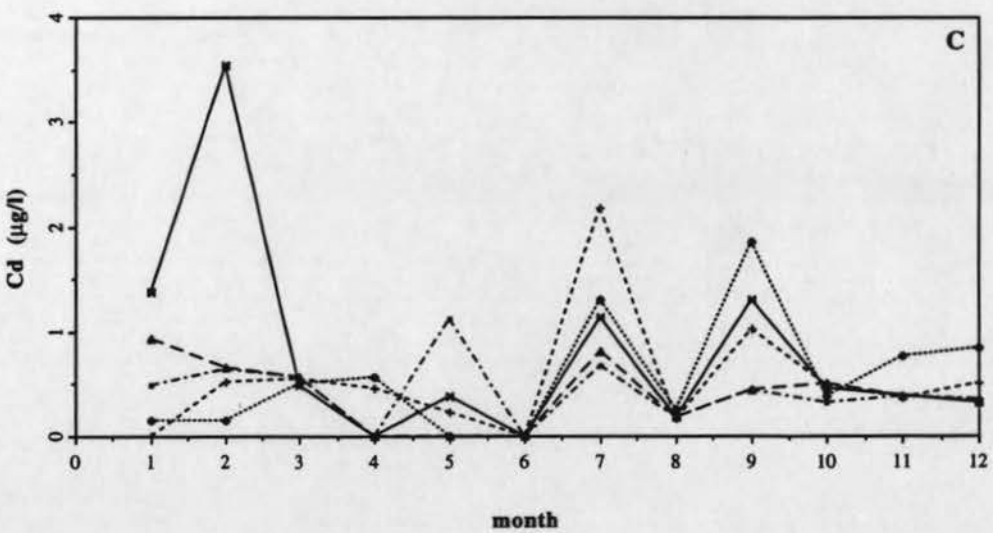
There is little evidence for eutrophication with the generally low concentrations of NO_2, NO_3 and PO_4, although there are occasional higher values which may cause concern in the short term.

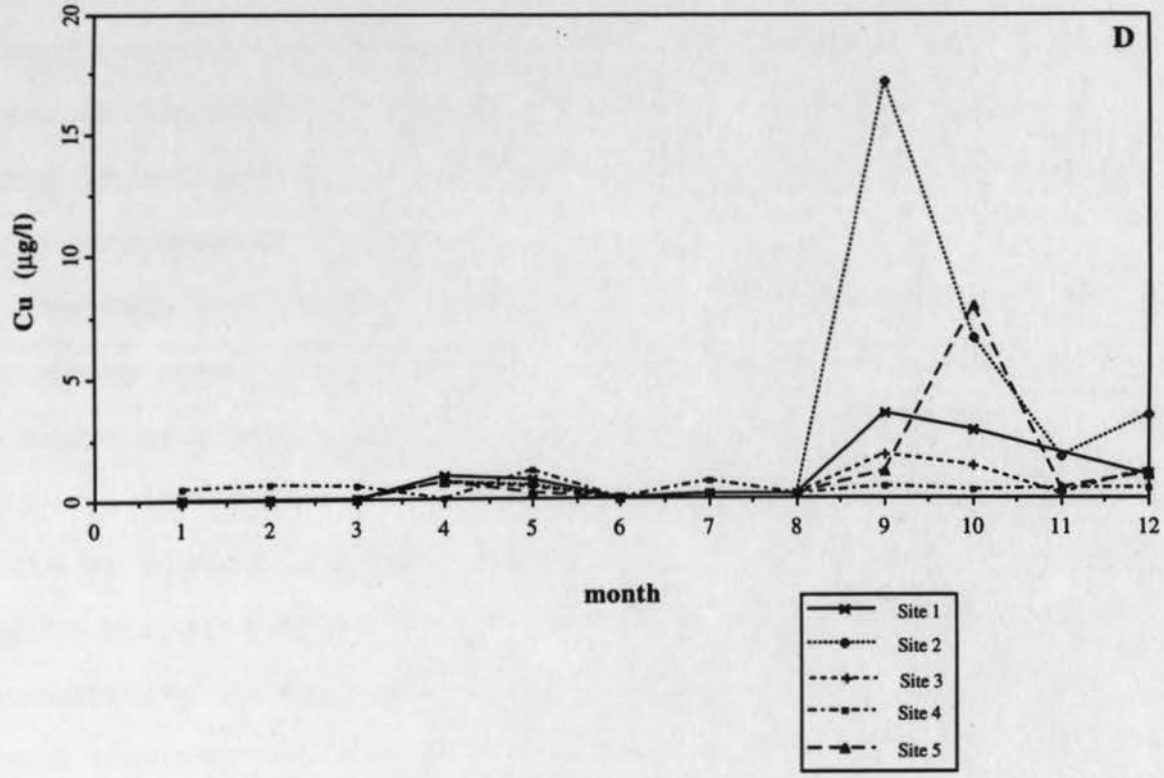
Heavy metals in the dissolved phase show similarities in trends. Zn (Fig 6.30 a) has generally lower values in the late spring, summer and early autumn with a maximum of 32 μg l^{-1} in June at site 2, the western inlet draining the industrial sub-catchment. Trends in Ni (6.30 b) generally mirror those of Zn with higher values in the late spring, summer and early autumn. Site 1, the eastern inlet, draining the predominantly agricultural sub-catchment, has the highest value of almost 9 μg l^{-1} in November. Cd (Fig 6.30 c) concentrations show little variability throughout the year, although there is a peak at site 1 of over 3.5 μg l^{-1} in November. Cu (Fig 6.30 d) remains fairly low for the first 8 months of the survey, but in the summer, particularly June, concentrations increase, values for site 2, the western inlet reaching a maximum of 18 μg l^{-1}. Trends for Pb (Fig 6.30 e) are for higher values in the

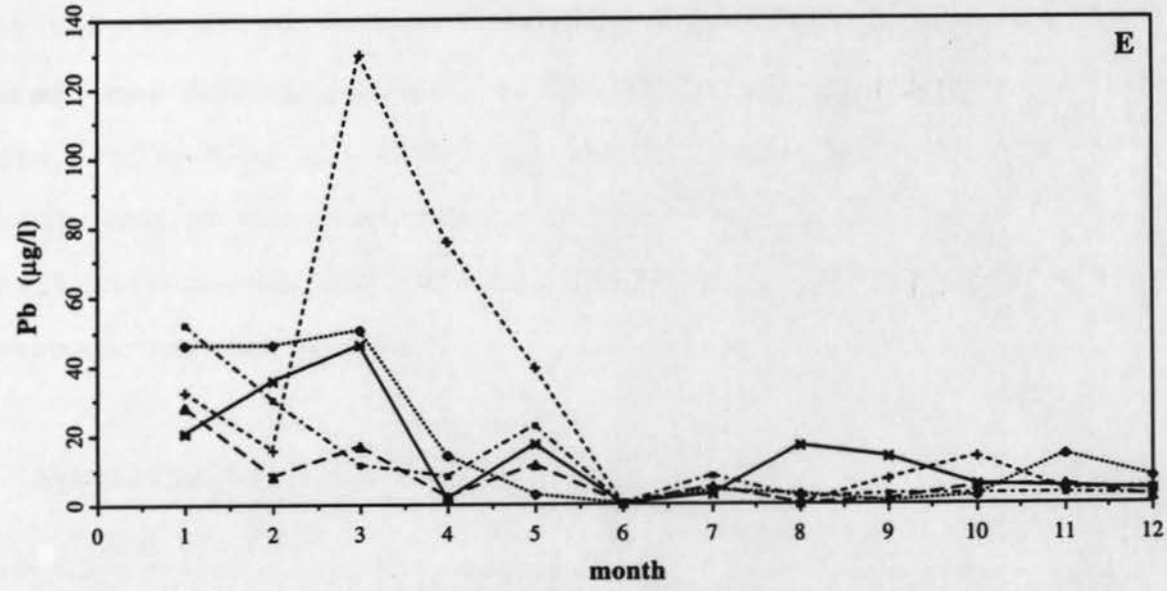
Fig 6.30 Wyken Pool monthly water quality monitoring, heavy metals
a. Zn b. Ni c. Cd d. Cu e. Pb








D
Cu (µg/l)
0
5
10
15
20
0
1
2
3
4
5
6
7
8
9
10
11
12
month
Site 1
Site 2
Site 3
Site 4
Site 5


E
Pb (µg/l)
0
20
40
60
80
100
120
140
0
1
2
3
4
5
6
7
8
9
10
11
12
month

winter, site 3 reaching a maximum of more than 130 $\mu g\ l^{-1}$ in December. In general, lowest values for all heavy metals are found in the spring, although concentrations in the dissolved phase are generally low.

Monthly monitoring of the water quality in Wyken Slough has shown some pattern due to seasonality, some is explainable in terms of the spring blooms of algae when Si and PO_4 decrease in concentration due to being incorporated in the tests of siliceous algae. Chapter 2.5 iii suggested that there may be a relationship between heavy metal concentration and productivity in the lake (Sigg, 1987) as falling particles would scavenge heavy metals from the water column. If this were the case, then dissolved heavy metal concentrations would be expected to be low in the more productive months, spring and summer, and higher in the winter. To a certain extent this pattern is shown by Cu and Ni but not by the other metals. Delivery of heavy metals to the lake through the western stream may dominate processes occurring within the body of the lake, reflecting the fact that urban environments are rarely stable due to constant change during construction work, initiation of new industry and changing patterns of vehicular movement through the area.

c. Stability of sinks

There is no evidence from the water quality monitoring of Wyken Slough during this study that mobilisation of heavy metals from the lake sediment or from the marsh is likely to be significant. The maximum concentrations of heavy metals in

the Wyken Slough catchment components and in the lake sediments are, however, enriched with respect to background values (Tables 6.3, 6.5, 6.20) and, as outlined above, urban catchments are rarely stable due to successive localised construction which tend to disturb small areas of the catchment each year (Douglas, 1985). This is reflected in the maximum values recorded in the NRA (Severn Trent Region) water quality data due to sporadic pollution incidents. Monitoring of this site was undertaken on a monthly basis and only for a period of 12 months. A more comprehensive monitoring programme needs to be established in order to assess environmental change in the long term before absolute conclusions can be drawn regarding the stability of the sinks of heavy metals.

6.8 Summary

This section is divided into two subsections in order to summarise the findings from this chapter, and also to take the opportunity to synthesise the findings from both research sites providing the basis for the calculations of budgets and yields in Chapter 7 and also for the discussion in Chapter 8.

a. Wyken Slough

Wyken Slough catchment is composed of four components; the marsh, streams, soils and water from the lake and the inflowing streams.

Analysis of the surficial marsh sediments show a complex pattern of heavy metal distribution which may be associated

with the role of the marsh as a filter, removing some of the metals before they reach the lake. This will be explored further in Chapters 7 and 8. Downcore, values higher than those in the surface sediments are found for Cd, Ni and Zn, whilst Cu and Pb have slightly higher values at the surface.

The heavy metals content of the streambed samples indicate that the main source of these contaminants is the western stream, particularly those tributaries draining the industrial estate. Areas of the eastern stream, particularly around the lorry park also exhibit high metal concentrations.

Apart from the lake sediments themselves, the soils contain the highest concentration of Pb of all the catchment components. The soil profiles indicate decreasing heavy metals concentrations with depth, with both cores having similar values for the individual elements.

Statistical analysis, particularly PCA, shows the close relationship between the catchment components. It also indicates the degree of colinearity between various parameters, particularly mineral magnetic properties, the consequences of which will be discussed further in Chapter 8.

The water analysis indicates that some pollution events have occurred in the past (NRA Severn Trent Region) but, during the monthly sampling exercise, fluctuations in the concentrations of the parameters tested mostly reflect seasonal changes.

b. Swanswell Pool, Wyken Pool and Wyken Slough

Both lakes show an increase in heavy metal concentrations from c 1850 to the present day. Table 6.5 gives the maximum concentrations of heavy metals in the lake sediments and compares these with the maximum values found in the catchment components of Wyken Slough. The magnitude of the enrichment of these sediments can be assessed by the calculation of enrichment factors (F) as explained in Chapter 4.2.4. This has been carried out on individual reaches of the streams flowing through Wyken Slough where it was found that the Bayton Road Industrial Estate exerted a great influence on the subsequent chemistry of the western stream, the lake sediments and the outflow. It was found, however, that concentrations at the outflow were demonstrably less than the inflowing western stream and it was suggested that heavy metals settled out in the lake before they were able to be transported through the outflow. Table 6.20 gives F values for maximum heavy metal concentrations from Swanswell and Wyken Pools and the Wyken Slough catchment components. All the elements show significant enrichment at both sites, in particular Zn and Cd in lake sediments and Zn in the Wyken Slough streams. F values for the River Sherbourne are also given in Table 6.20, and only in the case of Cd are the F values from the R Sherbourne higher than those from the Wyken Slough streams.

This comparison serves to illustrate the site-specific nature of the data obtained from lakes whose catchments have been subject to their own unique anthropogenic pressures. Jennett *et al*. (1980) suggest that due to the complexity of

the systems studied, heavy metal behaviour may be ecosystem-specific. Swanswell Pool is subject to atmospheric pollution from traffic and industry, as well as urban runoff from the surrounding buildings, roads and streets. Wyken Slough has many sources of pollution, but the major contributor appears to be the industrial estate with other sources from the nearby M6 motorway and landfill sites.

Table 6.20 Cultural enrichment factors at Swanswell and Wyken Pools and Wyken Slough compared with those from the River Sherbourne.

	1	2	3	4	5	6	7
Zn	55.4	24.4	77.8	14.4	31.1	24.4	4.55
Ni	2.6	5.25	20.0	10.0	10.5	7.8	1.18
Cu	20.0	10.0	17.0	3.5	1.5	23.5	4.17
Pb	11.0	17.5	5.3	8.3	5.75	7.5	3.12
Cd	75.0	15.0	7.5	3.5	25.0	10.0	19.5

1. Swanswell Pool lake sediments (n = 176)
2. Wyken Pool lake sediments (n = 237)
3. Wyken Slough stream bed sediments (n = 42)
4. Wyken Slough soils (n = 20)
5. Wyken Slough marsh core samples (n = 53)
6. Wyken Slough marsh, surface samples (n = 20)
7. River Sherbourne bed sediments (Thoms, 1987)

Chapter 7

Heavy metals and sediment budgets

7.1 Introduction

This Chapter presents the results of calculations performed in order to estimate the budgets of both the sediment and selected heavy metals in Swanswell and Wyken Pools which, together with the discussion in Chapter 8, address the aims and objectives set out in Chapter 1.3. The details of all calculations are found in Appendix 4.

In order to reconstruct the pollution history of the two research sites, sediment yields, accumulation rates and changing fluxes of heavy metals through time were calculated. Oldfield *et al*. (1983) emphasises the importance of calculating fluxes for an area in a certain length of time, rather than simply reporting heavy metals in terms of horizontal concentrations. According to Renberg (1986), a combination of concentrations and accumulation rates or fluxes provides the opportunity for more detailed interpretation.

However, difficulties with dating, discussed in Chapters 4 and 5, and the lack of time-synchronous horizons across the whole suite of cores, meant that they were only subdivided into two time zones; before and after the first occurrence of ^{137}Cs in the record representing about 1954. There was no opportunity to obtain a finer resolution of the temporal record by subdividing the record into shorter time increments (Foster *et al* 1985, 1987; Foster & Walling, 1994). Problems

with core correlation meant that it was impossible to correlate the depth of the first appearance of ^{137}Cs across the whole lake. Calculations were therefore based on average depths in cores which gives rise to two assumptions regarding sediment accumulation in both lakes:

1. The accumulation of sediment is constant either side of 1954. The results, particularly those from Wyken Pool (Chapter 5), indicate that plainly this is not the case. However, these calculations are presented as best approximations based on the evidence available and provide information on which to base further study.

2. There has been no heavy metal migration in the lake sediment. Chapter 2.6 indicated that evidence from other studies suggested that remobilisation in the sediment column may not be significant (Farmer *et al*, 1980; Alderton, 1985), but since this has not been specifically investigated in this study, the assumption has to be made that remobilisation is of minimal significance.

Metals are mainly associated with particulate matter and are transported in the lower atmosphere. In order to quantify historical changes in atmospheric pollution recorded in urban lake sediments, atmospheric dust records (Anon, 1982) were examined. Atmospheric dust is an important source of heavy metals when their flux in the hydrosphere is considered (Tisue & Fingleton, 1984; Schmidt & Andren, 1984). The transport and wet or dry deposition of atmospheric particulates depends upon

their particle size, or mode, (Quality of Urban Air Group, 1993), and therefore the distance of the site of deposition from the source of particulates is an important factor. The gradient of atmospheric dust fallout in the urban area was estimated using dust records (Anon, 1982) and these were compared with similar estimates for both rural Warwickshire and remote rural sites in the UK.

In order to identify the role of the drainage basin in the delivery of sediment and contaminants to the lake, stores of metals in the catchment components were calculated. These are important for an assessment to be made of the possible environmental damage should the metals be remobilised. Heavy metals budgets were therefore calculated and compared with data from nearby rural sites and with remote catchments in south-west England for which similar data are available.

The above calculations in part address the second aim which was to assess lake sediments as a source of proxy hydrological data over the last 100-150 years. The objectives associated with this aim were specifically concerned with the assessment of the paired lake-catchment system and with methodologies which will be addressed in the discussion in Chapter 8.

Sediment accumulation rates and yields to the two lakes are discussed first. This is followed by an estimation of the contribution to the two catchments of atmospheric dusts. Section 7.4 examines estimates of heavy metal accumulation rates. Finally, in section 7.5, an assessment of the role of the drainage basin in Wyken Slough is made and a comparison made of relative inputs from the catchment and the atmosphere.

7.2 Sediment accumulation rates and yields

Using the lake characteristics set out in Table 2.15, and the data for dry bulk density and depths of the sediment to 1850 presented in Chapters 4 and 5, the total dry sediment accumulated in both lakes was estimated (Table 7.1). All calculations are given in Appendix 4.

Table 7.1 Total dry sediment (minerogenic fraction) accumulated since 1850

	Swanswell Pool	Wyken Pool
Total (t)	1352.33	4760.44
Accumulation rate t yr^{-1}	9.45	33.29
Accumulation rate g cm^{-2} yr^{-1} of lake surface area	0.1326	0.148

A correction was made such that the data represents the minerogenic fraction only by subtracting the average organic matter component (9% in the case of Wyken Pool and 22% in the case of Swanswell Pool) from the total. The accumulation rate for each lake was calculated by dividing by the time elapsed since 1850 and the accumulation rate over the lake surface was calculated using the lake surface area given in Table 2.15. Whilst Wyken Pool contains more than three and a half times as much sediment as Swanswell Pool, the accumulation rate over

the lake bed is only slightly higher at Wyken Pool than Swanswell Pool since the lake area of Wyken Pool is over three times larger.

Average sedimentation through the life of the lake says nothing about the change in rate with time. The dated cores at Swanswell and Wyken Pools were therefore used to give a best approximation of the change in sediment accumulation rate and yield with time. All calculations are shown in Appendix 4. Table 7.2 shows the differences in sediment accumulation rates for period 1 (1850 - 1954) and period 2 (1954 - 1991). The sediment accumulation rate in Swanswell Pool increased by 235% from period 1 to period 2; in Wyken Pool it decreased by 21%. The decrease in accumulation rate in Wyken Pool probably reflects a combination of changing sedimentation and trap efficiency. Periods of construction work, particularly the housing estates built between 1919 and 1939 (Chapter 3.4.2) may have increased sediment yield in Period 1. In Period 2, construction of the Bayton Road Industrial Estate, the M6 motorway and the drainage ditch through the marsh may have increased sediment delivery, but has been followed by almost two decades of relative stability which may account for the lower overall sediment yield in Period 2. Trap efficiency is affected by changing hydraulic conditions (Foster *et al.*, 1990) such as improvement of drainage through the marsh. It is also affected by changing water chemistry and sediment properties such as particle size. It was shown in Chapter 5 that there may have been an influx of less dense sediment into the lake which may have been related to urbanisation within

the catchment, the changing nature of the sediment transported to the lake at this time may also have affected sediment yield.

The sediment yield was calculated for Wyken Pool which has a catchment area of 4.5 km^2. This could not be done for Swanswell which has no effective catchment. The results were compared with data from relatively undisturbed and cultivated catchments in North Warwickshire and are also given in Table 7.2.

The sediment yield calculated from sedimentation rates in Wyken Pool is similar to that of Merevale Lake. Since urbanised catchments are often associated with low sediment yields after the initial building and catchment disturbance phase is complete (Wolman, 1967; Douglas 1985) Wyken Pool would not be expected to have sediment yields higher than those for rural catchments such as Merevale. Seeswood Pool has higher sediment yields than Wyken Pool due to recent catchment disturbance caused mainly by agriculture including poaching by grazing animals and increased ploughing (Foster *et al.*, 1990). The yields for Wyken Pool are also less than the average for the Old Mill Reservoir (Foster & Walling, 1994) where sediment yields have increased in the last 50 years from 20 t km^{-2} yr^{-1} to 90 t km^{-2} yr^{-1} and average 54 t km^{-2} yr^{-1}, due to increased stocking densities and hedgerow removal. Changing land use within the catchment is reflected in changing sedimentation and, in the case of urban lakes, the high sediment yields following land clearance and subsequent construction are followed by lowered yields due to the covering of the land in concrete and tarmac (Wolman, 1967; Douglas, 1985). Swanswell Pool has no catchment and the sediment accumulation rate

Table 7.2 Comparison of sediment accumulation rates and yields for urban and rural sites.

	Period 1	Period 2
Accumulation rates (t $ha^{-1} yr^{-1}$):		
Swanswell Pool	7.88	18.47
Wyken Pool	15.419	12.14
Yields (t km^{-2} yr^{-1}):		
Wyken Pool	7.71	6.07
Merevale Lake[1] (9 time periods)	4 - 9	
Seeswood Pool[2] (11 time periods)	8 - 36	
Old Mill[3]	20 - 90	

[1] Foster *et al.* (1985)

[2] Foster *et al.* (1986)

[3] Foster & Walling (1994)

Accumulation rate reported in terms of lake surface area (ha)

Yields are reported in terms of catchment area (km^{-2})

reflects higher atmospheric fallout from vehicular particulate emissions, which have increased in the UK from a total of 30 kT in 1970 to nearly 70 kT in 1990 (Quality of Urban Air Group, 1993). Whilst the Quality of Urban Air Group, (1993) state that vehicular emissions probably have the most impact on the levels of pollutants at ground level, other sources such as commercial, industrial and domestic activities will also affect atmospheric particulate fallout. The following section considers the contribution of dust to the sediments of the two research sites and compares this with estimates from rural and remote rural sites.

7.3 Atmospheric dust contributions

The amount of atmospheric dust contributing to the two catchments can be estimated from Warren Springs dust records (Anon, 1982). The amount of dust falling on rural and remote rural sites have also been estimated and the results are set out in Table 7.3. The calculations involved are presented in Appendix 4.

The levels of dust falling on remote sites (70.3 kg ha^{-1} yr^{-1}) were taken to indicate background levels of atmospheric particulates over the UK. The urban dust levels were assumed to approximate those likely to be found at Swanswell Pool, with Wyken Pool approximating levels for the outskirts of a town. The gradient of fallout from the town centre to rural, and then remote sites, is also given in Table 7.3. Values for semi-urban and rural sites do not differ markedly although they are slightly lower in the rural area. Anthropogenic

Table 7.3 Amount of dust falling on urban, semi-urban, rural and isolated sites. Data from Warren Springs Dust Records (Anon, 1982).

Site description	dust fallout ($kg\ ha^{-1}\ yr^{-1}$)	Proportion relative to inner city sites (%)	Anthropogenic excess (%)
Area of old-fashioned housing	438	100	84
outskirts of town	341.3	78	79.4
rural	329	75	78.6
remote (west coast of UK)	70.3	16	0

excess indicates the proportion of dust falling on the sites above background and was calculated by assuming no anthropogenic excess at the remote sites. All calculations are given in Appendix 4. Here the variation between city centre, semi-urban and rural sites is not great, varying between 78.6 and 84%.

It is not possible to directly estimate the relative proportion of lake sediments being made up of atmospheric fallout since the effective net transfer efficiency of dust to

the lake is not known. Various estimates of the efficiency of the transfer of atmospheric dust to lakes have been made, and range from 10 to 25% (Schmidt & Andren, 1984).

7.4 Heavy metal accumulation values

As stated in section 7.1, metal concentrations downcore expressed in terms of $\mu g\ g^{-1}$ of dry sediment, do not convey an accurate picture of pollution history (Renberg, 1986), but in combination with metal annual accumulation values may provide more detailed and reliable results. This section therefore presents individual metal accumulation rates for both sites, and compares these with increases in the global use of heavy metals.

Temporal changes in heavy metal fluxes at both urban sites based on the two dated horizons are presented in Table 7.4. Fluxes of each heavy metal at both sites increase appreciably from Period 1 to Period 2. Zn shows the greatest increase at both sites, increasing by 7.5 and 5.6 times at Swanswell and Wyken Pools respectively. The metal increasing the least at both sites is Ni, showing a 3.4 times and 1.4 times increase at Swanswell and Wyken Pools respectively. The order of increase at the two lakes is otherwise slightly different:

Swanswell Pool : Zn > Cu > Pb > Cd > Ni
Wyken Pool : Zn > Cd > Cu > Pb > Ni

The increases in Zn and Pb at Swanswell Pool probably reflect increased traffic movements around the site, Zn from tyre wear

Table 7.4 Accumulation rates of heavy metals in Swanswell and Wyken Pools

	Swanswell Pool accumulation rate kg $ha^{-1} yr^{-1}$		Wyken Pool accumulation rate kg $ha^{-1} yr^{-1}$	
	period 2	period 1	period 2	period 1
Cd	0.1303	0.0338	0.2823	0.0979
Ni	1.035	0.305	3.4872	2.4464
Zn	29.367	3.936	6.2758	1.1297
Pb	5.27	1.138	2.017	0.8484
Cu	1.163	0.207	3.005	1.1501

period 1 = 1850 - 1954

period 2 = 1954 - 1991

and Pb from leaded fuels (Quality of Urban Air Group, 1993). Cu is mainly released by smelting and the burning of fossil fuel, although, as shown on Table 2.2, the weathering and flaking of paints and pigments and the breaking down and burning of treated wood are also important sources of this element. Cd and Ni reflect increased combustion of fossil fuels, although Cd would also be released from weathered paints and pigments (Table 2.2) as it is used to whiten paint pigments (Fergusson, 1990). The increases in Zn and Cd at Wyken Pool reflect the industry around the Pool which has included a Zn plating works and Ni - Cd battery factory (Chapter 3.4.2), but increases in all the heavy metals would arise from similar processes as mentioned above for Swanswell Pool with the difference that point sources from the catchment in the form of discarded items listed in Table 2.2 such as batteries, plastics and pharmaceuticals would also impact upon release of heavy metals to the environment. Whilst the sediment accumulation rate from 1954 in Wyken Pool has decreased in comparison to that pre-1954, all metal accumulation rates have increased, reflecting the contamination of the sediments that have been deposited in the last 37 years. None of the increases in the individual heavy metal accumulation rates at Wyken Pool, however, are higher than those shown at Swanswell Pool probably due to its city centre location, and hence higher atmospheric loading, and also the increased sediment accumulation rate in the last 37 years at the city centre site.

Chapter 2.5, (Table 2.1) shows that globally since 1900, anthropogenic emissions have become the most important source

of metals to the environment (Nriagu, 1990; Macklin, 1992). Table 7.5 compares the increase in heavy metal accumulation rates demonstrated for Wyken and Swanswell Pools and the global emissions rates. This demonstrates that the accumulation rates for the study sites are comparable or slightly lower for all metals except Ni which is considerably lower. The global emission rate includes that for industry as well as mining, and Table 5.5 demonstrated that areas subjected to the impact of mining produce concentrations of heavy metals in lake sediments an order of magnitude higher than those in urban lake sediments. Table 7.5 also includes the natural : anthropogenic ratios of heavy metal emissions, and demonstrates that the urban lakes exhibit increases in the accumulation rates of Cu, Ni and Zn which are higher than the published values, reflecting the central position they occupy for receipt of pollution by heavy metals. Departures from any published values may in part be a function of the different timescales involved, since the only dates available at both Wyken and Swanswell Pools were 1850 and 1954 and the data taken from Nriagu (1990) quoted values from 1900 to the present day. The differences between global and such site-specific data also reflects atmospheric and point sources at the regional and local scale and indicates the ecosystem-specific nature of such studies.

Differences in metal accumulation rates through time can reflect changes in the consumption : transport-related sources of heavy metals discussed in Chapter 2.5. The addition of tetraethyl lead (TEL) to fuel, as indicated in Table 2.3, and Quality of Urban Air Group, (1993), is the main source of Pb

Table 7.5 Global increase in the use of heavy metals since 1900 (Nriagu, 1990) compared with the increase in heavy metal accumulation rates at Swanswell and Wyken Pools from 1850-1954 to 1954-present.

	1	2	3A	3B
Cd	5.85	8.0	3.8	2.9
Cu	0.85	6.0	5.6	2.6
Pb	27.67	9.0	4.6	2.4
Ni	1.86	51.0	3.4	1.4
Zn	2.3	8.0	7.5	5.6

1. Ratio between anthropogenic (A) and natural (N) emissions of trace metals

2. Increase in global industrial emission rates, including mining

From Nriagu, 1990

3. Increase in heavy metal accumulation rate from 1850-1954 and 1954-1991 in:

A. Swanswell Pool

B. Wyken Pool

to the environment. Pb concentrations in the atmosphere fell by 77% between 1976 and 1989 due to initiatives to reduce the content of Pb in petrol (The Quality of Urban Air Group, 1993), however, Period 2 (1954-1991) encompasses the years when Pb emissions were at their highest and EC limit values were exceeded at some sites in the UK (Quality of Urban Air Group, 1993). Zn, on the other hand, is associated with the use, wear and disposal of various products (Table 2.2) and as such is an example of a consumption-related source (Brown *et al.*,1990; Macklin, 1992). Zn and Pb may therefore also be used as indicators of consumption and transport-related activities in the lake catchment.

Table 7.6 compares the accumulation rates of individual heavy metals presented in Table 7.4 with the accumulation rate for Zn as an indicator of changing metal use with time. At each site, the ratio increases post-1954, and in the case of Ni and Cu at Wyken Pool, pre-1954 levels of relative Zn accumulation were less than that of Cu and Ni; post-1954, the use of Zn has increased to such an extent that it is twice that of Ni and Cu. In most cases, the relative proportion of Zn accumulating in the sediments at both sites has doubled since 1954, and in the case of the comparison between Ni and Zn at Swanswell Pool, is nearly ten times the pre-1954 levels.

Table 7.6 The ratio of heavy metals to Zn at Wyken and Swanswell Pools.

	Swanswell Pool		Wyken Pool	
	1954 - 1991	1850 - 1954	1954 - 1991	1850 - 1954
	Period 2	Period 1	Period 2	Period 1
Zn:Pb	5.6	3.5	3.1	1.33
Zn:Cd	225.4	116.1	22.2	11.5
Zn:Ni	28.4	3.3	1.8	0.46
Zn:Cu	25.3	19.0	2.1	0.11

The Zn : Pb ratio has doubled post-1954, exemplifying that these data show that consumption-related activities have increased in relation to transport-related ones in these urban catchments. This is in direct opposition to the study by Tarr & Ayres (1990) of the Hudson-Raritan Basin, USA, in which the Zn : Pb ratio fell from 1880 to 1980 (Table 7.7). These data show that heavy metals results are ecosystem-specific, and particularly in the case of Coventry, reflect the general industrialisation which occurred in the area after 1900 (Chapter 3.2.3).

Table 7.7 Zn : Pb ratios from the Hudson-Raritan Basin from 1880 - 1980 (data from Tarr & Ayres, 1990)

	Average annual element emission (t)		
	Pb	Zn	Zn : Pb
1980	5312	7870	1.48
1970	9684	10225	1.06
1960	7203	8720	1.21
1950	4884	9170	1.88
1940	2504	8500	3.4
1930	266	7280	27.37
1920	74	5560	75.14
1900	92	1550	16.85
1880	29	470	16.21

A comparison has been made of these ratios with those of rural and remote rural sites (Foster *et al*, 1994), and these are presented in Table 7.8. The figures for Swanswell and Wyken Pools are the total flux of anthropogenic excess metals to the lake sediments. These data show that the fluxes of Pb and Zn to the urban sites are about ten times higher than that to rural areas which in turn are 3 - 3.5 times higher than the fluxes of Zn and Pb to the remote rural sites. The gradient of atmospheric fallout from urban areas to rural areas is fairly steep which suggests that whilst the dust records (Table 7.3) indicated that in general the fallout is slightly lower from

Table 7.8 Calculated atmospheric flux of Zn and Pb to catchment soils and lake sediments (kg ha^{-1}) from Foster *et al.* (1994).

	Zn	Pb	Zn:Pb ratio
A. Urban Midlands			
Swanswell Pool (lake sediments)	1045.0	900.0	1.16
Wyken Pool (soils)	132.6	42.0	3.16
Wyken Pool (lake sediments)	1313.0	700.0	1.88
B. Rural Midlands			
Merevale Lake (lake sediments)	90.0	12.9	7.14
Seeswood Pool (soils)	103.5	13.1	7.90
Seeswood Pool (lake sediments)	164.0	83.9	1.95
C. Remote rural			
Scilly Isles (lake sediments)	24.0	2.4	10.0

urban to rural areas, taking specific metals at specific sites shows that urban areas are in receipt of higher fluxes of

heavy metals than rural areas. It also suggests that the heavy metals are not exported in high concentrations any great distance from the urban to the rural areas. The ratios themselves also indicate that the anthropogenic excess Zn:Pb decreases with increasing urbanisation such that the urban sites have the lowest values and the rural sites have the highest values.

Best approximations of accumulation rates for the urban sites therefore show that the fluxes of heavy metals have increased since 1954 and that there is a gradient from the city centre, with high fallout, to the rural sites with appreciably lower values. The next section considers the distribution of heavy metals in the catchment components of Wyken Pool.

7.5 The role of the drainage basin

This section is divided into two subsections in order to consider both the quantity of heavy metals stored in the catchment of Wyken Slough and the proportions of atmospheric and catchment derived inputs.

1. The sinks of Pb and Zn in the catchment of Wyken Slough

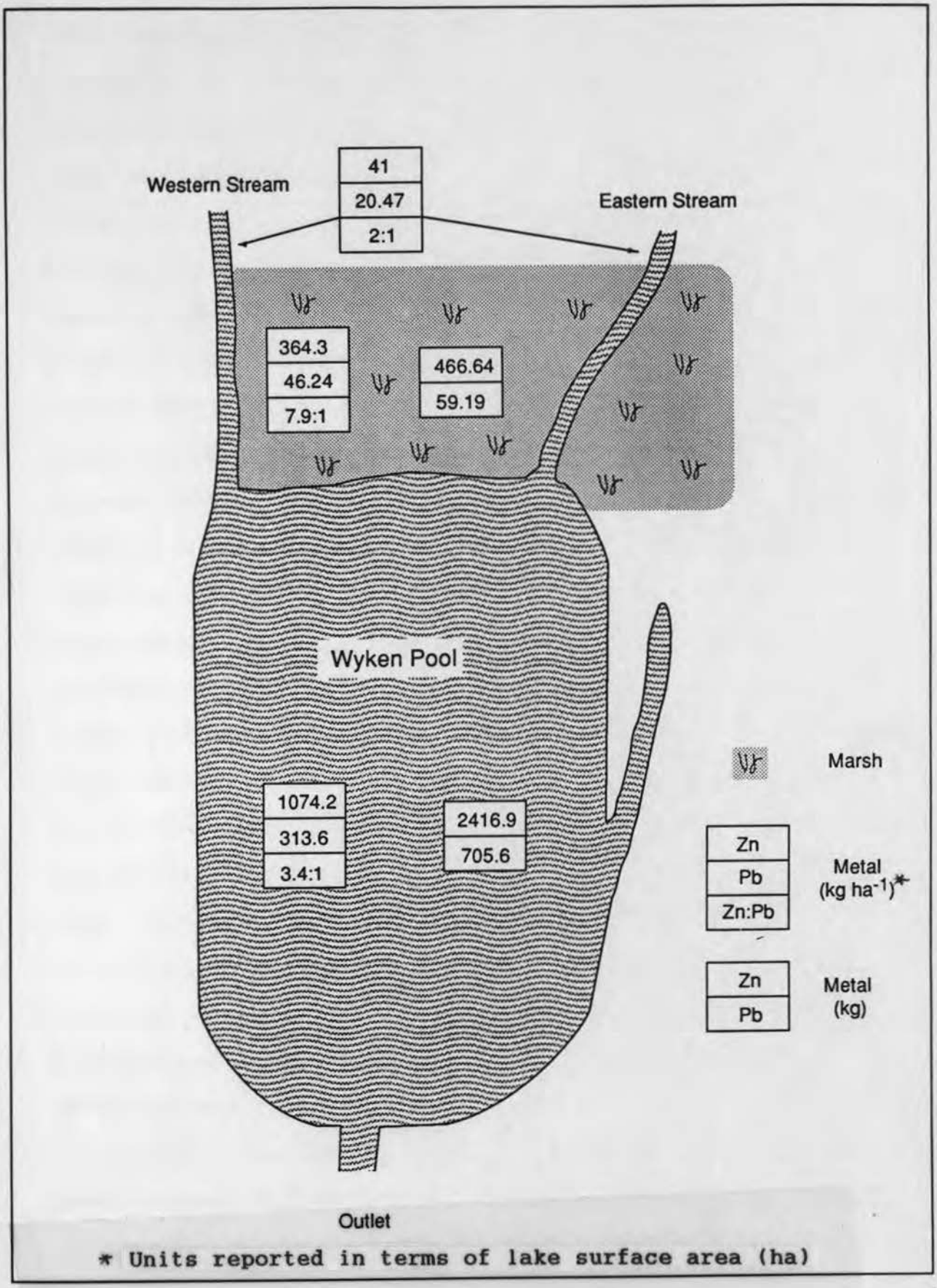
It has been shown that heavy metals are present in both Swanswell and Wyken Pool sediments in amounts appreciably above background (Tables 4.3 and 5.4). The concentrations measured in the Wyken Slough catchment were also found to be significantly above background levels (Table 6.20). There

would therefore appear to be significant amounts of heavy metals stored within the lake sediments and catchment components at both sites. This section presents previously published data in Foster & Charlesworth, 1995, which attempts to quantify the amount of Pb and Zn stored in the sediments of the lakes and catchment components. Pb and Zn were chosen to continue the theme of comparing the relative proportions of transport (Pb) and consumption (Zn) related activities in the catchments.

Fig 7.1 shows the amounts of both Zn and Pb stored in the sediments of Wyken Slough. There is a total of almost 3100 kg of Zn and over 800 kg of Pb stored in Wyken Slough, of which over 85% of the Zn and nearly 90% of the Pb is stored in the lake sediments. Adjusting for the background concentrations, values for which are presented in Table 5.4, about 70% of both Zn and Pb are related to anthropogenic activities since 1850 (Foster & Charlesworth, 1994). Should catchment conditions change, particularly with respect to pH and Eh, then these heavy metals at present stored in the sediments at Wyken Slough could be released into the environment. Should the Pool ever be dredged, then provision must be made for the safe handling of the dredged material as research has shown (Förstner & Wittman, 1981) that large amounts of heavy metals are remobilised in dredged materials and become a hazard to the environment. This is due to the exposure of anaerobic sediments to oxygen and the subsequent release of metals sorbed to particulates.

Fig 7.1 shows that the average Zn : Pb ratio for both streams is 2.1, and in comparison with similar ratios for the

Fig 7.1 Zn and Pb sinks in Wyken Slough (after Foster and Charlesworth, 1995)



* Units reported in terms of lake surface area (ha)

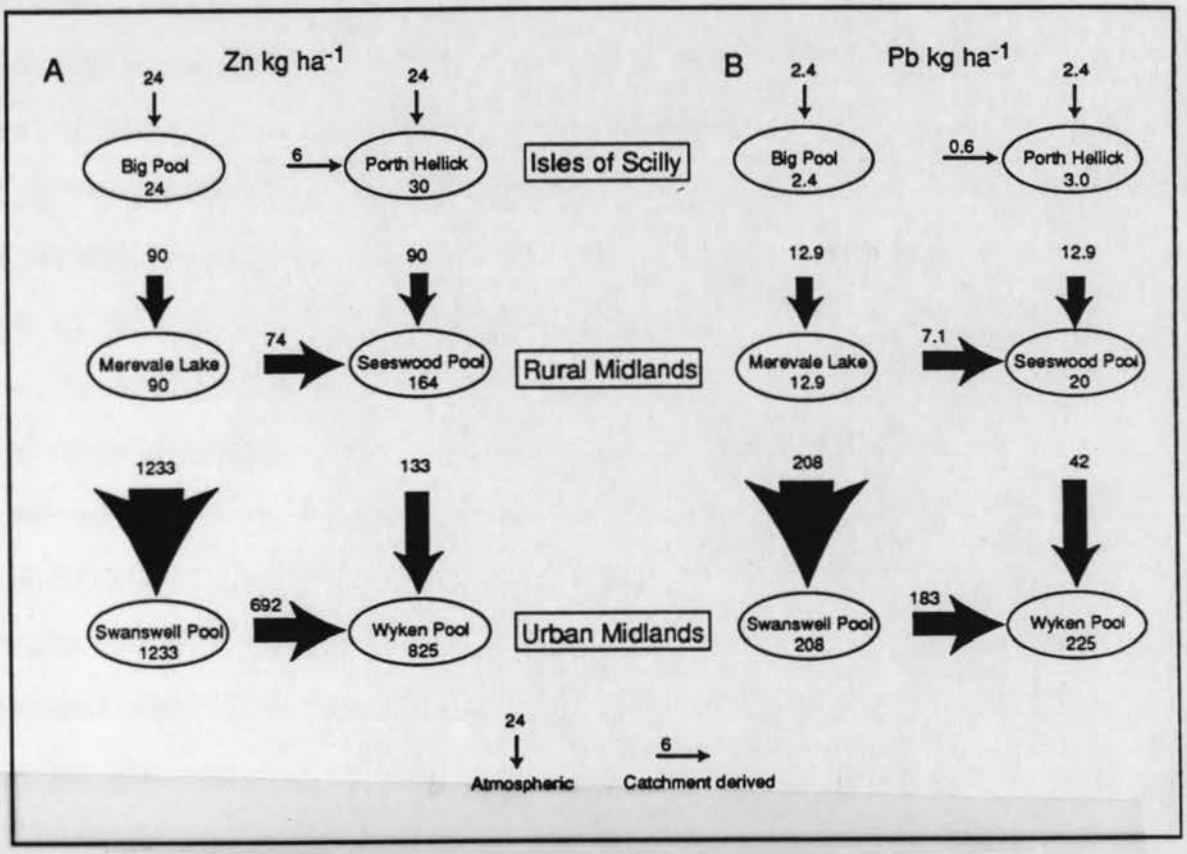
River Sowe (Foster *et al.*, 1994) it is comparable with other urban streams in the English Midlands. The ratio for the lake sediments is slightly higher at 3.4 and may reflect the high value for the marsh sediments of 7.9 which approaches those given for rural sites given in Table 7.8. The high value in the marsh indicates that these sediments are relatively more enriched in Zn than Pb. As discussed in Chapter 6.2 ii, research suggests that wetlands actively trap sediment and filter out certain pollutants (Williams, 1990) both physically by entrapment of particles on roots and stems and also metabolically. Williams (1990) states that plants such as the bulrush (*Schoenoplectus lacustris*) and common reed (*Phragmites australis*) actively take up heavy metals from the water. The efficiency of this process varies from 20 to 100% of total heavy metals carried in the inflowing streams. Chapter 2.5 iii discussed the partition coefficients (K_D) of various heavy metals between the particles and water. Table 2.10 shows that, whilst the K_D of Pb is not known with any great certainty, it appears to show a preference for the particulate phase. The K_D for Zn indicates that it has a preference for the soluble phase. The high Zn : Pb ratio for the marsh sediments may therefore reflect the different processes of transport of these two elements, the entrapment of Pb relying mainly on physical processes, whereas that of Zn relies more on metabolic processes.

However, more research needs to be carried out on the marsh vegetation before more than these tentative conclusions can be made.

2. Proportions of atmospheric and catchment input of heavy metals at Wyken and Swanswell Pools and their comparison with rural and remote rural sites.

Fig 7.2 is reproduced from Foster & Charlesworth, (1995), and shows the relative contribution of Pb and Zn from the atmosphere and from catchment derived sources for both Swanswell and Wyken Pools and from rural sites in the English Midlands and remote rural sites in the Scilly Isles. Site-specific atmospheric inventories were established using undisturbed catchment soils and lake sediments where there was no catchment derived influx (Foster *et al.*, 1994). Background metal concentrations (Table 5.3) were deducted from total values in order to calculate the anthropogenic excess. These data show that there is almost an order of magnitude increase in the atmospheric fallout of both elements from the city centre site (Swanswell) to the city-marginal site (Wyken Pool). There is also a strong gradient in fallout from the urban sites to the rural sites. Merevale Lake and Seeswood Pool lie to the north of the urban sites, some 18 km distant from Swanswell, and atmospheric fallout increases almost 14 times from the rural to urban sites. Chapter 2.5 discusses the deposition of airborne particulate-associated pollutants which can occur by either wet or dry processes. The residence times of particles in the atmosphere range from a few days to a week (Seinfeld, 1986) and their deposition depends on prevailing weather conditions as well as activities unique to the urban area such as the number of traffic movements and the orientation of buildings which will affect wind speed and

Fig 7.2 Anthropogenic excess heavy metal budgets for 6 lakes in lowland England
a. Zn
b. Pb



Units presented in terms of catchment area (ha)

direction (Quality of Urban Air Group, 1993). These data seem to support studies such as those by Johnston & Harrison, (1984) and Lygren *et al.*, (1984), which suggest that despite the residence times quoted above, the majority of pollutants, for example generated by road transport, are not dispersed far from their origin. Long distance transport of pollutants is obviously a factor, as studies by Macklin, (1992), and Tarr & Ayres, (1990) have shown, in that elevated levels of heavy metals have even been found in Antarctic ice cores. However, this study has shown that there is a steep gradient from the point of origin of the majority of metals to more remote areas, and that deposition of these pollutants within the urban area is their dominant means of removal. This is supported by the high proportions of heavy metals which are found within the catchment as opposed to that found in the atmosphere. The heavy metals derived from catchment sources increases appreciably from 20% in the remote rural sites to 35 - 45% in the rural sites and 81 - 84% in the urban area.

These data therefore suggest that heavy metals are not transported far from their site of origin, but are deposited within the urban area, where they provide the most important source of metal pollutants to urban lake sediments.

7.6 Summary

Problems with dating have only enabled the heavy metal profiles from each pool to be divided into two time periods, post-1954 and pre-1954. However, this has enabled comparison to be made of the sediment accumulation rates and yields and

the heavy metal fluxes and yields. This has shown that whilst the sediment accumulation rate at Swanswell Pool has increased by over 200%, that at Wyken Pool has decreased by over 20%. The decrease at Wyken Pool may be due a combination of changing sedimentation associated with construction within the catchment, and changing efficiency of the lake to trap sediment. The heavy metal accumulation rates for all metals have increased post-1954 at both sites and for all metals. In spite of the decrease in sediment accumulating at Wyken Pool post-1954, most metals show a doubling of their accumulation rates from Period 1 to Period 2. Increase in heavy metal accumulation rate at Swanswell Pool is higher (at Swanswell Pool) than Wyken Pool, commensurate with the increasing deposition of contaminated sediment at the city centre site.

Calculations of the atmospheric contribution to these sites has enabled comparison to be made between urban, rural and remote sites with the result that deposition increases by an order of magnitude from remote rural to urban sites.

At the catchment scale, fluxes of heavy metals have been calculated which have indicated the possible role of the wetlands in regulating some of the elements before they reach the lake, but more work is required before more than tentative conclusions can be made. Sinks of heavy metals have been identified in the various compartments at Wyken Pool and, should environmental conditions change, remobilisation of these sinks would provide a considerable environmental hazard.

Comparison of atmospheric and catchment derived metals at Swanswell and Wyken Pools with rural and remote rural sites indicate that the urban area provides the primary source of

heavy metals and also the primary sink for heavy metals. The proportion of metals exported from the urban area is small in comparison with the amount retained and deposited there.

Chapter 8 provides a discussion of this study and also ways in which it can be built on in future work.

Chapter 8

Discussion

8.1 Introduction

The two principal objectives of this study were introduced in Chapter 1.3. These were:

1. To reconstruct the history of atmospheric, point source and diffuse heavy metal pollution in an urban environment.

2. Evaluate the lake-sediment record as a source of proxy hydrological data over the last 100-150 years.

In order to achieve objective 1, an attempt has been made to:

1. Quantify the historical changes in atmospheric pollution as recorded in the sediments of Swanswell Pool.

2. Quantify the historical changes in the heavy metal content of lake sediment derived from a slowly industrialising catchment (Wyken Slough) over the last 150 years and to identify the role of the drainage basin in the sediment delivery process.

3. Quantify the relative contribution of atmospheric and catchment derived contaminants in Wyken Slough.

In relation to objective two, an attempt has been made to:

1. Evaluate the use of paired lake-catchment studies in reconstructing pollution histories over short to medium timescales.

2. Identify the practical limitations of utilising a range of environmental tracers (heavy metals, environmental magnetism and radioisotopes) for identifying contaminant sources.

This chapter addresses the aims and objectives of this study and also identifies areas in which further work is required.

8.2 Reconstructing urban pollution histories

Documentary evidence and the physical and chemical analysis of water, soil and sediments from both sites were used to identify the impact of urbanisation on heavy metal contamination. Chapter 3 demonstrated that industrialisation began later in Coventry than in other parts of the UK, but after about 1900, the population grew rapidly and the urban area expanded. It was also shown that both of the research sites had undergone substantial changes to their catchments in the past; although the last major change to Swanswell Pool (which was probably constructed in the mid-thirteenth century) occurred in 1850 with the culverting of its' major inflow, the Springfield Brook. The following sections evaluate the first objective, by considering the record of heavy metal

contamination in urban lake sediments as a means of reconstructing the pollution history.

8.2.1 Trends in lake sediment chemistry

Analysis of cores from each lake indicates that the concentration of heavy metals in the lake sediment have increased markedly upcore. This trend has been recorded in other UK lake sediments particularly in sites at some distance from urban and industrial centres such as Llangorse Lake, in south-central Wales (Jones, 1984; Jones *et al.*, 1991) and upland tarns in Wales, the English Lake District and the Galloway region of Scotland (Batterbee *et al.*, 1988). Upcore increases in heavy metal concentration at remote sites over the last 130 years is a reflection of the sensitivity of lakes and their sediments to the long range transport of atmospherically derived metals. The record appears to be particularly well preserved in lakes with low sedimentation rates such as Llangorse Lake, which has a sediment accumulation rate of 59 cm^{-1} in the 100 years post-1840 (Jones *et al.*, 1985). Whilst upcore increases in heavy metal concentration appear to occur in many lake sediments, this is not always true, particularly if the sedimentation rate or dominant sediment source changes through time (Foster and Dearing, 1987). The sediments of Wyken and Swanswell Pools, however, both exhibit upcore increases in heavy metal concentration, but comparison of cultural enrichment factors (F) with other lakes subject to industrial and urban pollution (Table 5.4) shows that the urban environment produces a

unique, ecosystem-specific reaction dependent on the sources of the heavy metals in the catchment.

However, a general lack of comparative studies in urban areas indicates the need for research in this environment.

Sequential digestion of lake sediments has provided important information concerning the likely long term stability of heavy metals incorporated in the sediment. Some fractions exhibited little change upcore. In the case of Swanswell Pool (Table 4.5), this was mainly in the residual fraction, whereas at Wyken Pool, little change was found in the exchangeable fraction (Table 5.7). The dominant fractions in both lakes for all heavy metals were Fe and Mn oxides and organic matter. These findings support those found in other studies of lake sediments, such as Lake Coeur d'Alene, Idaho, USA, which has been affected by recent mining activity (Horowitz *et al.*, 1993). The implications of the speciation of heavy metals in terms of management concerns are further discussed in section 8.4.

8.2.2 Quantification of historical changes in pollution as recorded in urban lakes and identification of the role of the drainage basin.

Chapter 7 assessed the relative significance of atmospheric and catchment sources in contributing to the heavy metals content of lake sediments. It was found that there was almost an order of magnitude increase in the atmospheric fallout from a city marginal (Wyken Pool) to a city centre site (Swanswell Pool). However, comparison with remote rural

(Isles of Scilly) and rural sites in the Midlands (Foster *et al.*, 1994) showed that the proportion of heavy metals derived from catchment sources increases appreciably from less than 20% in remote areas, to between 35 and 45% in rural areas and between 81 and 84% at the urban sites. Sinks of heavy metals were also calculated and, whilst they are stored in the stream sediments and in the marsh, the bulk of the metals are stored in the lake sediments. In the case of Wyken Pool, 85% of the Zn and 90% of the Pb were calculated to be stored in the lake sediments, with the remainder stored in the marsh and fluvial sediments.

The two streams flowing into Wyken Pool drain a catchment with a wide variety of heavy metal sources. The urban environment is different from areas where a small number of point sources have contaminated the environment, as is often the case with historical and contemporary mining activities (Harding & Whitton, 1978; Elner & Happey-Wood, 1980; Dearing, 1992; Horowitz *et al.*, 1993) where contamination is local to the mine. The difficulty in the case of urban lakes is in discriminating between these many different sources. Fig 7.1 identified the sinks of heavy metals in the Wyken Pool catchment and showed that both the marsh and the inflowing streams represent important repositories of pollutants. With 15% of the Zn and 10% of the Pb stored in the stream and marsh sediments, remobilisation of the heavy metals and their transport to the lake some time in the future is a possibility. The following sections therefore examine the environmental consequences of the computations made in Chapter 7 regarding the storage of heavy metals.

a. Streams

Table 6.2 compared published values of heavy metal concentration in rivers subjected to various activities with those of the Wyken Slough Brook. This showed that the enrichment of stream sediments with heavy metals in urban areas is significant, as much as 66.7 for Cu in the Bayton Road reach of the Wyken Slough Brook (Table 6.4), but that, as noted by Förstner (1983), values for streams passing through mining areas are very much higher. Table 6.2 showed that whilst the concentration of Zn and Ni are the same in both urban and mined areas, that of Pb is nearly 40 times higher, Cu 15 times higher and Cd almost 3 times higher in the mining areas than in urban areas. On the basis of a river reach analysis, it was found that the Eastern stream of the Wyken catchment exhibited very little enrichment in comparison to the other reaches, but that heavy metal concentration in the stream draining the Industrial Estate was significantly above background (Tables 6.3 and 6.4). Table 6.3 also showed that metal concentrations in the outflow stream were lower than those in bed sediments of the western stream, but still higher than background for all heavy metals except Pb. Heavy metals are therefore being lost through the outflow. Although an analysis of stream sediments is not directly relevant to the problem of reconstructing pollution history, it has an important contribution to make in detecting sources (Förstner, 1983). This study has highlighted the importance of an industrial estate as a source of heavy metals and that the lake is not the only sink for all the anthropogenic excess

metals. This has important management implications, further explored in section 8.4.

b. Marsh

The concentration of heavy metals in sediment cores taken from the Wyken Slough marsh increase upcore, but the spatial distribution of heavy metals is complex and is probably associated with the distributory channels running through the area. Enrichment factors (Table 6.20) indicate that all heavy metals are significantly higher than background in the marsh sediments, with values of between 1.5 and 31.1 for Cu and Zn respectively. Zn and Ni were more enriched than in the lake sediments and Zn, Ni, and Cu were more enriched than in the fluvial sediments. Studies of incorporation of heavy metals in marsh sediments, such as those by Glooschenko *et al.* (1981) and Harding & Whitton (1978) have identified similar trends in marsh areas where anthropogenic activity is also a major influence on sediment geochemistry.

Analysis of the marsh sediments in this study, and of the marsh plants at Wyken Pool by Ambridge (1989), indicated that the marsh is acting as an important filter, either systemically taking up some of the heavy metals into living tissue or trapping the particles in stems and roots before they can reach the lake. In Chapter 7 it was suggested that Zn, being more soluble than Pb, is preferentially taken up by the marsh vegetation, which may explain the greater enrichment of Zn relative to Pb in the marsh sediments. Any interference with the marsh, as happened in the 1970's when the City

Council drained and culverted the western part of the area, will facilitate the removal of contaminated sediment from the marsh as well as allowing the direct delivery of heavy metals from catchment sources into the Pool. Several studies (Harding & Whitton, 1978; Glooschenko *et al.*, 1981; Gambrell *et al.*, 1982; Baker *et al.*, 1990; M^{c}Grath *et al.*, 1993) have indicated the beneficial effects of marsh plants in isolating heavy metals from the environment (Chapter 2.8ii). It would thus seem reasonable to suggest that future management should not involve further draining of the marsh, but should investigate the means of its reinstatement in order to improve the quality of water and reduce sedimentation rates in Wyken Pool.

Analysis of the marsh sediments in this study provided information on the sinks of heavy metals as well as the recycling of pollutants through vegetation. It also provided information on a means of "cleaning" (M^{c}Grath *et al.*, 1993a) inflowing waters before they reach the lake.

The analysis undertaken at the Wyken Slough has therefore shown that not all the heavy metals derived from catchment sources actually reach the lake. Fig 7.2 shows, however, that almost 3 times as much Zn is stored in the lake sediment than is stored elsewhere in the catchment and almost 5 times as much Pb is stored in the lake sediments as is stored in other components of the fluvial system. In the case of Wyken Pool, therefore, whilst it must be accepted that a proportion of the pollutants do not reach the lake and some are lost through the outflow, the majority are incorporated in the lake sediments.

8.3 Evaluation of the lake-sediment record as a source of proxy hydrological data over the last 100-150 years

Foster & Charlesworth (1995) recognised three processes which influence the preservation of the record of heavy metal pollution in lake sediments. These were the effectiveness of metal scavenging processes, trap efficiency and post-depositional stability.

The effectiveness of heavy metal scavengers such as organic matter and Fe and Mn oxides (Förstner & Wittmann, 1981) influences the ability of the sediment column to retain the heavy metals record. Traditionally, the Fe : Mn ratio has been used as a palaoenvironmental indicator of changing redox conditions, (Foster & Walling, 1994). Examination of the Fe, Mn and organic matter profiles from Swanswell Pool do not indicate a major change in redox conditions or a significant increase or decrease in the amount of organic matter delivered to the sediments. However, the Fe : Mn ratio and other properties of the sediment from Wyken Pool, such as bulk density, the non-metallic element concentration and particle size, indicate a change in the sediment delivered rather than a change in environmental conditions associated with Eh (Chapter 2.11 iii). In this case, therefore, it would appear that the change in Fe : Mn ratio is associated with the change in sediment delivered rather than any change in redox. It would appear that scavenging processes and post-depositional stability provide conditions suitable for the incorporation of heavy metals into the lake sediment.

Trap efficiency affects the ability of the lake to trap sediment and the associated heavy metals load. Chapter 2.3 discussed the problems inherent with urban lakes, such as Swanswell Pool, without a catchment, and Wyken Pool, with an artificially enlarged channel network due to the presence of storm drains. It is clear that future work should attempt to quantify the trap efficiency of Wyken Pool which could be done by the installation of continuous monitoring equipment at the inflow and outflow to estimate trap efficiency.

Evidence for post-depositional stability of the heavy metal record was derived from mineral magnetic measurements in which there is no loss of susceptibility or change in the S-ratio towards the mud-water interface which might be indicative of changing stability within the sediments (Anderson & Rippey, 1988).

Although absolute dating estimates of metals loadings through time are confounded by problems with trap efficiency and spatial variability in the sedimentary record, data appear to provide a qualitative record on which to base interpretation of trends in pollution history, particularly in the absence of long-term hydrological data. The following section considers the use of a paired lake-catchment in this study to reconstruct environmental change, and Section 8.3.2 assesses the methodologies used in this study.

8.3.1 The paired lake-catchment system

A paired lake catchment study is a means of providing a comparison between ecosystems impacted by similar processes

(Foster *et al.*, 1987), such as urbanisation and industrialisation. The contrast in this case was in providing a site where sources of heavy metals were mainly atmospheric in comparison with a site with a complex and multi-source catchment. Swanswell Pool has, therefore, provided data on atmospheric loadings to an urban area, but results indicate that it is still not a simple model. Evidence of the complexity of the processes was provided by the lack of a relationship between mineral magnetic characteristics and heavy metal concentrations in the lake sediments in the face of published evidence of significant magnetic-metal relationships in urban street dusts (Beckwith *et al.*, 1984; 1986; 1990; Stott, 1986). This is discussed further below.

At Wyken Slough, it was not possible to discriminate between the various sources, although the Zn:Pb ratios given in Chapter 7 do give some indication of the consumption: transport-related ratios of sources in the urban area. Comparison of Pb and Zn loadings of the urban sites with rural and remote rural sites (Chapter 7.3), enabled the spatial impact of pollution to be assessed. A strong gradient of atmospheric fallout was found, in that the urban sites contained an order of magnitude greater heavy metal loadings than rural sites which contained an order of magnitude more than those in remote rural locations. However, a fallout gradient was also found at the local scale. It was shown by extrapolation from Warren Springs Dust Records (Anon, 1982), that there is more potential for dust accumulation in the city centre site than the city marginal site (Table 7.3). The dust fallout at the city marginal site was found to be 78% of that

in the city centre. This pattern is also reflected in heavy metal budgets (Fig 7.2) in which anthropogenic excess Zn was found to be 1.5 times higher in the city centre than in the suburbs. Pb budgets were found to have similar values at both sites, reflecting the more uniform distribution of transport-related pollutants throughout the urban area.

The relative importance of diffuse atmospheric inputs from local, regional and long-range sources and the multiple point and diffuse sources within the catchment will vary from catchment to catchment. Sites used in a paired lake-catchment system study in an urban area therefore need to be chosen with care; the urban area is one of complex interrelationships, depending ultimately on the degree to which anthropogenic activity impacts upon it.

8.3.2 Patterns through time? An assessment of methodology

In Chapter 2.10ii two reasons were given for the collection of data on heavy metal concentrations in the two catchments. The first was to assess the total amount of heavy metals in the sediments to enable fluxes and accumulation rates to be calculated. The second was to enable partitioning of the metals and hence to assess bioavailability. Both methodologies appear to provide valuable information, although the fractionation was time consuming and hence only one core per lake was sequentially digested. In Chapter 2.10e it was suggested that magnetic properties might be used as a surrogate for heavy metal analysis. The lack of correlation between heavy metal and mineral magnetic properties in the

lake sediments is demonstrated in Chapters 4 and 5. This is further compounded by the lack of consistent correlation found between the two sets of properties in both lakes and in any of the catchment stores at Wyken Slough. PCA (Chapter 6) supports this view as the explained variance is split between heavy metals, which generally represent factor 1, and mineral magnetic properties which correlate with factor 2. Tables 4.6 and 5.8 give the coefficients of variation (CV) at 2 standard deviations for the various properties measured in the sediments at both sites. These are much higher downcore than spatially for heavy metals, indicating that these are a reasonable representation of pollution trends. Mineral magnetic characteristics, however, have similar spatial variability to that of downcore variability and hence may reflect sorting, or the presence of magnetotactic bacteria or greigite rather than trends through time. It would seem, therefore, that the mineral magnetic properties of sediments incorporated into these urban lake basins do not provide a suitable surrogate for heavy metal concentrations.

However, in Chapter 2.10.ie, previous research was reviewed which showed a good correlation between mineral magnetic characteristics and heavy metals in the sources of urban street dusts (Revitt *et al.*, 1981; Hunt *et al.*, 1984; Beckwith *et al.*, 1986; Brilhante *et al.*, 1989; Beckwith *et al.*, 1990). Sediments are mixtures of materials and most of these studies were confined to specific sources, such as power station fly ash and motor vehicle emissions (Hunt *et al.*, 1984). The components of such mixtures may be synergistic or antagonistic (Jennett *et al.*, 1980) and the incorporation of

one element may alter the properties of the whole. Beckwith *et al.*, (1986) list four sources of mineral magnetic particles in an urban catchment:

1. atmospheric sources
2. particulates derived from the soil
3. particulates derived from vehicles, both as a result of emissions via exhaust gases and also from paint and rust from corroding bodywork
4. sources from the materials making up the surrounding road and paved surfaces.

It would be over-simplistic to assume that these particulates are transported to the lake essentially unchanged. Beckwith *et al.*, (1986) found that there were complex mixing processes occurring during transport with generally constant deposition from the atmosphere in the catchment and variable amounts from the other three sources. These mixing processes will continue with the incorporation of sediment into the lake. Sequential digestion of the sediments from both lakes has shown the preferential concentration of heavy metals in both organic matter and Fe and Mn oxides. Organic matter, as well as quartz and calcium carbonate, are notable for being diamagnetic (see Table 2.22), and Thompson & Oldfield (1986) consider them to be diluents. Enhanced magnetic signals may occur due to growth of magnetic minerals in the lake sediment which may be due to bacterial activity (Farina *et al.*, 1990; Mann *et al.*, 1990; Stolz *et al.*, 1990) or to the presence of authigenic magnetic minerals such as greigite (Snowball & Thompson, 1988). Both of

these sources could provide a magnetic signal unrelated to the deposition of heavy metals.

Bacterial magnetite would be single domain since it is contained within a bacterial organelle or magnetosome (Thompson & Oldfield, 1986; Farina *et al.*, 1990). Such small particle sizes would be reflected in high a χ_{fd} (Thompson & Oldfield, 1986). Figs 4.15c and 5.14c show that higher Xfd is found in the top few cm of the sediment cores from each lake suggesting that biogenic magnetite may be present in the upper sediments.

The poor relationship between mineral magnetic characteristics and heavy metals is also found in the soils, marsh and fluvial sediments. It would appear that the solid deposits studied at both sites are a result of complex mixing processes involving a combination of three sources:

1. the urban sources highlighted by Beckwith *et al.*, (1986) in which there may be a relationship between magnetic properties and heavy metals.

2. biogenic and authigenic magnetic minerals in which there is no associated anthropogenic heavy metal presence.

3. heavy metals transported on diamagnetic material such as organic matter or calcium carbonate in which there is no magnetic mineral association.

Two of the three sources are therefore composed of material in which there is no original connection between

magnetic minerals and heavy metals. Future work to differentiate between these sources is required in order to fingerprint a range of sources. This analysis could be used to ascertain the proportion of sediment-associated heavy metals with or without a mineral magnetic signal.

Chapter 2.10ii also suggested that the magnetic characteristics of lake sediments in urban lakes could be used to correlate synchronous horizons in a suite of lake sediment cores, but this has proved problematic. As suggested above, the lower downcore variability in the magnetic property compared with its spatial variability suggests that magnetic particle incorporation might be dependent on the characteristics of the individual lake basin and may not accurately represent a lake-wide depositional pattern within the same basin. In this case, therefore, mineral magnetic properties are of less use than visual stratigraphic characteristics such as the differentiation between the red clay and black organic gyttja at Swanswell Pool.

Magnetic characterisation, however, provided some information regarding changing sources through time. The scattergrams of χ_{lf} versus SIRM suggested that the sources of sediment at Swanswell Pool changed at the red clay / black gyttja boundary, and at Wyken Pool that the sources had not appreciably changed since ca.1850.

Further to the discussion of the optimisation and accuracy of different coring strategies discussed in Chapter 2.8, the PCA plots of the individual catchment components (Figs 6.24 a-d), indicate that coring position seems to have little effect on the location of sediment core data in the Principal

Component Space and therefore on an environmental interpretation. The locations of the envelopes delineating catchment components and lake cores from the four coring positions are very similar suggesting that there is little difference between the four cores and that, in the case of Wyken Pool, one core would be representative of the whole lake sediment sequence.

Partitioning of metals according to particle size proved problematic in that, as Horowitz (1991) suggests, it is difficult to define what is meant by a particle. A long chain of organic matter or a clump of particles cemented together by Fe and Mn oxides do not constitute discrete particles in the geomorphological sense, but this study has shown that Fe and Mn oxides and organic matter are important sinks of heavy metals in the urban environment. More research needs to be carried out on this aspect, which is further discussed in Section 8.4.

Dating of the sediments was problematic in that the ^{137}Cs signal appeared to be well preserved in the sediment, but that of ^{210}Pb was not. Varvas & Punning (1993) found ^{210}Pb unreliable in their dating of four contaminated Estonian lakes, suggesting catchment disturbance and post-depositional mobility of ^{210}Pb related to redox conditions at the mud-water interface as important factors. However, these conditions do not explain the apparent stability of ^{137}Cs in the sediment column. Lack of detector time led to coarse resolution of the samples that were analysed, which may be part of the reason for the discrepancy, but no other explanation is apparent. The ^{137}Cs data could be corroborated by other techniques such as

examination of the sediment for carbonaceous particles which has been used successfully by a number of workers to date lake sediments (Griffin & Goldberg, 1981, 1983; Renberg & Wik, 1984, 1985, 1986; Batterbee *et al.*, 1988; Wik *et al.*, 1986; Rose, 1990; Rose & Batterbee, 1991; Wik & Renberg, 1991). However, none of these other studies have to date focused on urban lakes and the problem would probably be the large amount of these particles in the sediment which might make counting difficult (N Rose, pers comm).

The use of elements such as Fe and Mn to infer palaeo-redox conditions (Oldfield, 1977) may need closer examination since at Wyken Pool, concentrations of these elements seem to reflect changing sedimentation due to disturbance in the catchment, rather than any change associated with redox conditions in the lake.

The lakes therefore retain an archive of pollution history in the form of slowly accumulating sediments and the paired lake-catchment system provides a framework with some degree of experimental control. Assessment of the use of other sediment characteristics as a surrogate for heavy metal analysis, such as mineral magnetic measurements, has shown that the urban environment produces a complex mixture of material. The problems with some of the methodologies, such as dating, has meant that the resolution of the temporal record has been rather coarse, but this study has shown, nonetheless, that interpretation of the pollution history of urban lakes is possible. The following section discusses how the results of this study could be applied to the management of contaminated urban sites.

8.4 Management implications

The drainage basin provides the means for both the transport of pollutants and for their storage. Sediments providing the store for heavy metals in turn can become a source should environmental conditions become favourable for their remobilisation.

This study has shown (Chapter 7.5) that there are high concentrations of heavy metals in the fluvial and limnic sediments of Swanswell and Wyken Pools. Harrison (1987) and Horowitz (1991) suggest that the greatest threat to the environment is by active sediments either as suspended sediment or as entrained sediment. Chapter 2 outlined the environmental conditions under which remobilisation and release of previously bound heavy metals might occur. Water quality and sediment analysis in this study would indicate that, whilst there is a large quantity of heavy metals bound up in the sediments in both lakes and in the catchment of Wyken Slough, there is no immediate threat to the environment due to remobilisation of metals. However, urban environments are rarely stable, in that there is constant change due to construction work, initiation of new industry and constantly changing patterns of vehicular movement through the area. Monitoring of the individual urban catchment for environmental change and the formulation of management strategies to prevent further pollution by new sources and by remobilisation of historical ones appears to be a priority.

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Appendix 1

Refereed Publications

Foster I.D.L., J.A. Dearing & S.M. Charlesworth (1987) Paired lake catchment studies: a framework for investigating chemical fluxes in small drainage basins. *Applied Geography*, 7, p 115 - 133.

Foster I.D.L., S.M. Charlesworth, J.A. Dearing, D.H. Keen & H.Y. Dalgleish (1991) Lake sediments: a surrogate measure of sediment associated heavy metal transport in fluvial systems? *IAHS Conference Report*, Vienna 1991, p 321 - 328.

Charlesworth S.M. & I.D.L. Foster (1991) Pollution, rescue and management: the problem of two shallow urban lakes, Coventry, UK. *IAHS Conference Report*, Vienna 1991.

Foster I.D.L., S.M. Charlesworth & D.H. Keen (1991) A comparitive study of heavy metal contamination and pollution in four resevoirs in the English Midlands, UK. *Hydrobiologia* 214, p 155 - 162.

Charlesworth S.M. & I.D.L. Foster (1993) The effect of urbanisation on sedimentation: the history of two lakes in Coventry, UK. In Duck & M^{c} Manus (eds) "Reservoir geomorphology & sedimentology". Wiley, Chichester.

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Foster I.D.L. & S.M. Charlesworth (1995, in press) Heavy metals in the hydrological cycle : Trends and explanations. *Hydrological Processes*.

Foster I.D.L., S.M. Charlesworth & S.B. Proffitt (1994) Sediment-associated heavy metal distribution in urban fluvial and limnic systems; A case study of the River Sowe, UK. In *"Particulate matter in rivers and estuaries"*. Proc. Hamburg Conf., IHP.

Reports

Foster I.D.L., S.M. Charlesworth & D.H. Keen (1988) An evaluation of the quality and character of Wyken Slough and of its bottom sediments. *Sediments and Water Group Report*, Coventry Polytechnic.

Foster I.D.L., S.M. Charlesworth & D.H. Keen (1988) The sedimentology and water balance of Swanswell Pool, Coventry. *Sediments and Water Group Report*, Coventry Polytechnic.

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Foster I.D.L. & S.M. Charlesworth (1990) Heavy metal pollution in the Wyken Slough- an appraisal of the problem and identification of the sources. *Centre for Environmental Research and Consultancy*, Coventry Polytechnic.

Foster I.D.L., S.M. Charlesworth & J.A. Dearing (1990) The Quinton Pools, Coventry: a hydrological and sedimentological study. *Centre for Environmental Research and Consultancy*, Coventry Polytechnic.

Appendix 2

Analytical procedures

1. Field and laboratory handling of cores

Cores taken in core tubes were sealed by means of rubber bungs and plastic tape in the field and transported back to the laboratory in a vertical position. Those taken in Russian corers were placed in plastic guttering, sealed in polythene tubing and sealed for transport back to the laboratory.

Mackereth core tubes were extruded as soon as possible upon return to the laboratory. Any cores that could not be extruded immediately were placed in a constant temperature cabinet. Russian cores were cut into 2 cm slices by means of a palette knife and samples were placed into clean, labelled, plastic petri dishes for the sediment to be described. Cores were described immediately after extrusion to avoid contamination or oxidation, which may have altered the appearance of the sample.

2. Bulk density

The field wet samples were placed in clean, dry, preweighed and labelled petri dishes. The petri dishes containing the samples were then reweighed and placed in an oven at 45° C until dry. Once dried, the samples were removed from the oven and allowed to cool when they were were reweighed and their wet and dry bulk densities calculated.

3. Loss on ignition

After drying and grinding, between 1 and 3g of the sample was placed in a preheated and cooled, weighed crucible with lid. The sample was placed in a muffle furnace at 550° C for 2 hours. The crucible was then removed from the muffle furnace and allowed to cool in a dessicator for 2 hours, reweighed and then placed in the muffle furnace at 850° C for 4 hours. It was allowed to cool and reweighed. Loss on ignition wascalculated from weight loss up to 550° C, and carbonate content from the weight loss between 550° C and 850° C.

4. Mineral magnetic measurement

The oven dried and ground sediment was packed into a preweighed, labelled 10 ml plastic pot. The sediment was be packed firmly into the pot to ensure that the sediment did not move. The pot and sediment were weighed and any space between the top of the sample and the pot lid was filled with sponge to prevent movement of sediment during measurement.

Magnetic susceptibility at low and high frequency was measured using a Bartington Instruments MS2 Susceptibility Meter.

Saturated isothermal remanent magnetisation (SIRM) was measured at 0.8 tesla followed by a reverse field of -0.1 tesla (IRM). The field was applied to the sample with a Bartington Instruments Molspin pulse magnetiser.

5. Chemical analysis

a. Total digestion

Approximately 1g of oven dry sediment was weighed accurately to four decimal places into a clean, dry, labelled 50 ml Kjeldahl flask. 1 ml perchloric acid, 5 ml nitric acid and 1 ml sulphuric acid were carefully pipetted into the flask in a fume cupboard and 3-4 glass anti-bumping beads added. A control was set up in the same way but without sediment. The flasks were moderately heated on a Kjeldahl stand until white fumes were evolved and the residue turned white to creamy yellow. If the residue remained brown, a further 1 ml of perchloric acid was added and the flask heated more strongly.

When the reaction was complete, the solution was diluted with about 20 ml deionised water and boiled for 5 minutes. It was allowed to cool and then filtered through a pre-weighed, dried, GF/C Whatman glass fibre filter paper. The filter funnel and glass beads were both carefully rinsed with deionised water. The filter paper was dried in an oven at 40° C overnight and then reweighed to estimate the solid residue.

The filtrate was decanted into a 100 ml volumetric flask and the Buchner flask was carefully rinsed with deionised water into the volumetric flask. 3 ml of lanthanum chloride (LaCl) solution containing 26.6g LaCl 100 ml^{-1} were added to stop interference when measuring for calcium by AAS and the solution made up to 100 ml with deionised water. The solution was stored in a clean, labelled polypropylene bottle in the refrigerator until analysed. Due to deterioration of the

sample, analysis was undertaken within a fortnight, but was usually carried out within a few days.

In order to test for analystical variability, a lake sediment sample was taken and subjected to total digest and AAS analysis for heavy metals 6 times. The results are shown in Table 2.1A.

Table 2.1A Replicate analysis of heavy metals to test for analytical variability (ug g^{-1}).

sample number	Cd	Ni	Zn	Pb	Cu
1	48.95	58.74	3259.91	636.32	127.26
2	38.93	67.52	3173.23	621.54	125.39
3	49.6	59.53	3204.68	644.91	128.98
4	48.37	58.05	3115.33	625.62	135.45
5	39.84	67.72	2818.73	647.01	129.48
6	39.28	58.92	2779.14	640.12	137.84

Phosphorus

5 mls of filtrate were pipetted into a clean 50 ml volumetric flask and approximately 25 ml of deionised water added. 5 ml ammonium molybdate-sulphuric acid solution and 5 ml stannous chloride were added and the solution made up to 50 ml with deionised water. The contents of the flask were mixed thoroughly. Calibration standard were made up in the same way

as the samples by adding 0, 0.5 and 1 ml stock phosphorus solution to the flasks giving concentrations of 0, 0.025 and 0.05 mgP respectively. The flasks were stood in the dark for the colour to develop for 20 minutes.

An LKB Ultraspec was set up to read at a wavelength of 640nm, the 0 mgP standard was used as a blank to set the baseline and the 0.025 and 0.05 mgP standards were used to give the calibration curve. The absorbance for standards and samples were read immediately after the 20 minute colour development time as the colour so produced is not stable.

Using BBC software, the calibration curve was plotted and the concentration of phosphorus read off, the amount of phosphorus per gram of sediment could then be calculated.

Reagents

Ammonium molybdate solution

Dissolve 5g ammonium molybdate in 300 ml deionised water. Add 61 ml concentrated sulphuric acid and make up to 500 ml with deionised water. Keep cool in a dark bottle.

Stannous chloride solution

Dissolve 0.25g stannous chloride in about 200 ml deionised water. Add 2.225 ml concentrated hydrochloric acid and make up to 250 ml with deionised water. Make fresh when rquired.

Phosphate stock solution

Dissolve 0.2195 g dried potassium orthophosphate (KH_2PO_4) in a litre of deionised water containing 1 ml concentrated sulphuric acid to prevent the growth of mould.

b. Sequential digest

The methodology and reagents are outlined in Tables 2.2A and 2.3A.

c. Determination of heavy metals

The instrument used to determine the concentrations of heavy metals was a Varian 1475 atomic absorption spectrophotometer (AAS).

The operating conditions for the elements concerned are listed in Table 2.4A.

The instrument gives results in mg l^{-1} by comparing against a set of known standard concentrations. The concentration in mg g^{-1} can then be calculated.

6. Dating

Counting was carried out in the Physics Department of Coventry University using an EG and G Ortex planar crystal which is a low efficiency HPGe, low energy photon spectrometer. ^{137}Cs was measured at 661.64 KeV, ^{210}Pb at 46.5 KeV and ^{214}Pb at 351.92 KeV. Ground, oven dried samples were

Table 2.2A Sequential extraction methodology. (After Tessier *et al.*, 1979)
(For reagents, see Table 2.3A)

Fraction (See Table 2.27b)	Method
1.	About 1.0g of oven dried sediment was added to 8 ml 1M sodium acetate adjusted to pH 8.2 in a centrifuge tube. It was agitated continuously for 1 hour and then centrifuged at 4000 r.p.m. for 15 minutes. The supernatant was decanted with a pipette and retained for analysis. The residue was retained for Stage 2.
2.	The residue from Stage 1 was leached at room temperature with 8 ml 1M sodium acetate set to pH 5.0. It was agitated continuously overnight to remove carbonates. It was centrifuged and decanted as Stage 1.
3.	The residue from Stage 2 was extracted with 20 ml sodium dithionite solution for 1 hour in a water bath at maximum temperature with occassional agitation. It was centrifuged and decanted as in Stage 1.
4.	The residue from Stage 3 was extracted with: i.) 3 ml 0.02M nitric acid + 30% hydrogen peroxide adjusted to pH 2 with nitric acid. It was heated to 85°C in a water bath for 2 hours agitating occassionally. ii.) 3 ml 30% hydrogen peroxide set to pH 2 with nitric acid and heat to 85°C for 3 hours agitating occassionally. Allow to cool. iii.) 5 ml 3.2M ammonium acetate (to prevent the adsorption of metals onto the oxidised sediment) in 20% (v/v) nitric acid, diluted to 20 ml with deionised water. Agitate continuously for 30 minutes. Centrifuge and decant as Stage 1.
5.	Wash the residue from Stage 4 into a clean, dry labelled, 50 ml Kjeldahl flask and add 1 ml concentrated sulphuruc acid, 5 ml nitric acid and 1 ml perchloric acid and treat as a total digest (see p 14).

Table 2.3A Reagents for sequential digest.

Fraction	Reagent	Recipe
1.	1M sodium acetate pH 8.2	77.08 g l^{-1} with ammonia solution
2.	1M sodium acetate pH 5	as above with acetic acid
3.	sodium dithionite solution	0.3M sodium dithionite (72.639 g l^{-1}) + 0.175M sodium citrate (51.47 g l^{-1}) + citric acid (5.25 g l^{-1}) made up to 20 ml.
4 i.) iii.)	0.02M nitric acid 3.2M sodium acetate	1.26 ml l^{-1} 246.7 g l^{-1}

counted for 12 hours, mainly because this was the only window in a series of on-going experiments in which they could be measured. If 12 hours was insufficient or the percentage error was too high, further counts were made on top of the original counts until enough had been obtained. ^{137}Cs, ^{214}Pb and ^{210}Pb were counted simultaneously.

Table 2.4A Operating conditions for the AAS

element	wavelength	lamp current	slit width
calcium	422.7	3	0.5
magnesium	202.6	3	1.0
sodium	589.0	0(E)	0.2
potassium	769.9	0(E)	0.5
iron	386.0	5	0.2
manganese	279.5	5	0.2
cadmium	228.8	3	0.5
nickel	232.0	3	0.2
zinc	213.9	5	1.0
lead	217.0	5	1.0
copper	324.7	4	0.5

7. Measurement of particle size: the Malvern 2600 Laser diffractor.

The samples were pretreated to remove organic matter. The sediment was placed in a clean, dry, labelled beaker and 50 ml

100 vol hydrogen peroxide added in a fume cupboard. The supension was swirled carefully in the beaker to mix and the reaction observed. If it was violent an equal amount of deionised water was added. The beaker was placed on a hot plate at about 90° C and left until the reaction had stopped (up to several days depending on the sample).

When the reaction was complete, the sample was transferred to a 50 ml polypropylene centrifuge tube and spun for 5 minutes at 300 r.p.m. The supernatant was decanted using a pipette and the pellet washed in deionised water. The sediment was washed and centrifuged three times in total. The pellet was then suspended in a small amount of water, transferred to a plastic petri dish and placed in an oven at 40° C until dry.

When dry, the sample was ground in a pestle and mortar ready to be flushed through the M2600 Laser Granulometer. The dispersant used was tap water with mechanical agitation in an ultra sonic bath until the readings were steady (1-3 minutes). A 63 μm lens was used throughout which measures in the range 1.2-118 μm .

Appendix 3

Table 3.1A Wyken Slough Brook bed sediment descriptions

a. Stream 1

Sample N°	Description	Munsell N°
1.	Plant material with pebbles and sandy clay	7.5/YR/5/4 brown
2.	Plant material, sandy. High organic matter content	10/YR/2/2 very dark brown
3.	Plant material with clay and grit. High organic matter content.	10/YR/2/2 very dark brown
4.	Plant material with sand and high organic matter content	10/YR/2/2 very dark brown
5.	Slate and brick rubble, quartz pebbles, little organic matter	10YR/2/2 very dark brown
6.	Silty, fine grained, no plant material	10/YR/2/2 very dark brown
7.	Plant material with black organic patches. Silty.	10/YR/2/1 black
8.	Mainly fine, silty sediment with some plant material and organic patches	10/YR/2/2 very dark brown
9.	Pebbles, some grit, some plant material	10/YR/2/1 black and 10/YR/2/2 very dark brown
10.	Very gritty with very fine red brick rubble, no plant material	10/YR/2/1 black

Table 3.1A (continued)

b. Toxic Tip

Sample N°	Description	Munsell N°
1.	Gritty with some plant material sticky, glutinous.	10/YR/2/1 black
2.	Greasy, oily, gritty with an unpleasant odour	10/YR/2/1 black
3.	Silty with some plant material	10/YR/2/2 very dark brown
4.	Muddy with some plant material	10/YR/2/2 very dark brown
5.	Silty with plant material and an unpleasant odour	10/YR/2/1 black
6.	Plant material including roots greasy	10/YR/2/2 very dark brown

c. Bayton Road

1.	Pebbles with finer grained sediments and brick rubble. Some plant material	10/YR/3/2 very dark greyish brown
2.	Very gritty with brick rubble and metal waste, some larger pebbles with finer grained material. Oily odour.	10/YR/2/1 black
3.	Sandy/silty texture with some pebbles. Some plant material	10/YR/3/2 very dark greyish brown
4.	Grit and clay. Strong smell of oil. Some plant material.	10/YR/2/1 black
5.	Some grit and sand with small pebbles, but mainly plant detritus and rubbish.	10/YR/5/3 brown

d. Outflow

	Sandy with black organic matter and plant remains	10/YR/2/1 black

Table 3.1A continued

e. Stream 2

Sample N°	Description	Munsell N°
1.	Sandy clay. Not organic	7.5/YR/5/4 brown
2.	Sandy with stones and brick rubble and plant material	7.5/YR/5/4 brown
3.	Sandy grit with small areas of organic matter	10/YR/2/2 very dark brown
4.	Large pebbles and brick rubble No rganic matter or plant debris	10/YR/4/3 dark brown
5.	Silty sand with some brick rubble plant material and some organic matter	10/YR/2/2 very dark brown
6.	Silty, withplant material and organic material	10/YR/2/2 very dark brown
7.	Fine grained, greasy with an unpleasant odour. Plant debris and organic matter	10/YR/2/1 black
8.	Gritty with pebbles. Some plant material, little organic remains.	10/YR/4/3 dark brown
9.	Sandy gravel with brick rubble. Some plant debris, shells and crustacean remains	10/YR/2/2 very dark brown
10.	Gritty sand with pebbles. No plant remains and little organic matter.	10/YR/3/4 dark yellowish brown
11.	Sandy silt with some plant debris	10/YR/2/2 very dark brown
12.	Sandy with a high proportion of plant remains	10/YR/2/2 very dark brown
13.	Silty with plant material	10/YR/2/2 very dark brown
14.	Sandy with stones and plant remains	10/YR/2/2 very dark brown

Table 3.1A (continued)

e. Stream 2

15.	Sandy grit with brick debris and some plant material	10/YR/2/2 very dark brown
16.	Sandy with pebbles and some plant material	10/YR/4/3 dark brown
17.	Sandy silt with some orange brick debris. Little plant remains	10/YR/2/2 very dark brown
18.	Plant debris with pebbles, some larger stones and orange brick debris.	10/YR/4/3 dark brown
19.	Sandy organic sediment with plant remains	10/YR/2/2 very dark brown
20.	Silty organic sediment with plant remains	10/YR/2/2 very dark brown
21.	Mainly brick rubble, with little plant remains	10/YR/2/2 very dark brown

Table 3.2A Marsh Core 2 sediment descriptions

Depth (2 cm intervals)	Description	Munsell colour
1	Dark brown organic silt with leaves	5Y/3/2 reddish brown
2	"	"
3	"	"
4	"	"
5	"	"
6	"	"
7	Dark brown/black sediment with roots	5Y/3/1 very dark grey
8	"	"
9	"	"
10	"	"
11	"	"
12	"	"
13	Very dark grey silt	"
14	"	"
15	Dark grey silt with red clay lenses	"
16	"	"
17	"	"
18	"	"
19	"	"
20	"	"
21	"	"
22	"	"
23	"	"
24	Friable, dry	"

SEVERN TRENT WATER
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My Reference: PR/HW/A/SO/WY/G
L

Your Reference:

27th November 1987

Dear Sirs,

Wyken Slough Brook.

I refer to your letter dated 10th November 1987, in connection with the quality of the watercourse which runs through Wyken Slough.

I enclose, herewith, data relating to the routine sampling point upstream of the Slough, where comprehensive information is available. Up to April 1982, regular data were obtained at a point downstream of Bayton Road Industrial Estate but, due to a reorganisation in 1982, sampling was switched to a different point, although this site effectively represents the quality of the stream. Data for these points are also enclosed.

There is only one regular trade effluent discharge on the Bayton Road Industrial Estate, which passes to the watercourse. This is from Abbey Panels and consists of oil-contaminated cooling water. The Company operate a treatment plant and the effluent entering the watercourse consistently complies with the limits of the consent imposed by the Authority. Until 1984, the foul sewage pumping station serving Bayton Road Industrial Estate was regularly subjected to ingress of storm water which in turn, caused overflow to the stream. Since that time, pollution has only resulted from intermittent spillage, save for the normal deterioration caused by rainfall run-off on an urbanised area.

No detailed information is available about the materials deposited at the Hawkesbury Tip, in that the tip was active in a period when little control was exercised over such sites and current legislative requirements on recording and notification were not enacted. The materials deposited are believed to have been by-products and waste materials from Courtaulds factories in the city, mainly of an organic nature. Leachate/drainage from the site passes through a treatment plant and samples are regularly taken of the discharge to the watercourse. Although there is obviously variation in the quality, the effluent is generally of an acceptable standard.

Cont/...

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Mr. P. Ramsden.

ENCLOSURE

In summary, this watercourse is generally of an acceptable quality for an urban stream and, although regular discharges to it are satisfactory, it is inevitably vulnerable to spillages, particularly in its head waters.

Yours faithfully,

p.p. Dr. B.D. Waters
Divisional Scientist.

COURTAULDS

15th December 1987

Dr. I.D.L. Foster,
Department of Geography,
Coventry Polytechnic,
Priory Street,
Coventry CV1 5FB

Dear Dr. Foster,

I acknowledge receipt of your letter of 11th December 1987 re Wyken Slough.

It is correct that Courtaulds have used the Hawkesbury Tip for the disposal of materials but not since 21st September 1979. It is also the case that from 1974 the site was owned by J & H B Jackson and we only tipped there under licence which stipulated (inter alia) that Jackson hereby convenants with the Licensee (Courtaulds Ltd.):

(a) to maintain or cause to be maintained the treatment plant installed at the premises so as to prevent the discharge of any polluted overflow

(b) to take or cause to be taken all necessary measures to prevent the waste deposited at the Property by the Licensee causing a nuisance to the neighbouring owners and occupiers

(c) to indemnify the Licensee against all actions claims and demands which may arise out of the tipping at the Property by the Licensee

(d) to comply at its own cost with any statutory or any other regulations for the time being in force relating to the deposit of industrial waste and to obtain any permission or Licence necessary for such operation and in particular any Licence required under the Protection of the Environment bill if enacted.

Regretfully we have discovered no records before that date but it would appear that Jacksons must have records relating to the control of the site and would point to any likelihood that an outflow would be deleterious to the Wyken Slough.

As a guide to what was tipped the agreement between Jackson and Courtaulds contained a schedule, copy attached. (Spanzelle was our elastomeric fibre and Teklan/Courtelle are variants of our acrylic fibre).

Since 1979 our wastes have been disposed of outside the Coventry area.

Yours sincerely,

J. Mackenzie

Dr. J. Mackenzie
Site General Manager

Enc:

Courtaulds plc
PO Box 16 345 Foleshill Road Coventry CV6 5AE (0203) 688771 Fax: (0203) 687325 Telex: 312171
Registered in London No. 128124 Registered Office 18 Hanover Square London W1A 2BB

SCHEDULE

Effluent Sludge

being: semi-dry solids extrtacted from effluent liquor and consisting substantially of Cellulose, Zinc Hydroxide, Carboxymethyl Cellulose and Calcium Sulphate.

D.F. & V.L. Spanzelle Waste

being: substantially liquid viscose, wet and dry fibrous wastes, solidified Spanzelle dope, Alkali Cellulose and various other wastes - the composition of which will be notified at least one month in advance and will not be tipped until an appropriate Licence has been obtained from the relevant Statutory Authority under the Town and Country Planning Acts or any other Act amending replacing or adding to that Act for the protection of the Environment, arising from time to time from new processes.

S.F. Lab./D.C.E. Wastes:

being: substantially Teklan/courtelle wastes, Amino Ethyl Cellulose and various other wastes - the composition of which will be notified at least one month in advance and will not be tipped until an appropriate Licence has been obtained from the relevant Statutory Authority under the Town & Country Planning Acts or any other Act amending replacing or adding to that Act for the protection of the Environment, arising from time to time from new processes.

Appendix 4

Calculations of dust

The Warren Springs dust records (Anon, 1975), Swanswell was taken to be equivalent to an "Area of dense old fashioned housing" and Wyken Pool to be the "outskirts of a town". To complete a gradient from an urban city centre to rural areas and to remote rural areas, a value of 329 kg ha^{-1} yr^{-1} for the rural site at Merevale Lake was taken from Foster *et al.* (1990) and a value for a site equivalent to a remote rural area was taken from the Warren Springs tables as an "area in open country". Table 4.1A gives the calculations.

Using the equivalent of Swanswell Pool (area of old-fashioned dense housing) as representing a site receiving 100% dust fallout, then the gradient across the urban, semi-urban, rural and remote rural areas can be calculated. These calculations are shown in Table 4.2A.

To calculate the amount of dust falling on Swanswell and Wyken Pools per year, the total amount of sediment in each lake was calculated. The results are set out in Table 4.3A. From Table 4.3A the amount of dust falling on the surface of the lake per year is 438 kg ha^{-1} yr^{-1} (Swanswell Pool) and 341.3 kg ha^{-1} yr^{-1} (Wyken Pool).

Table 4.1A Calculations of dust falling on urban and rural areas

	Area of old-fashioned housing	outskirts of town	open country
Average daily mg m^{-2} dy^{-1}	120	93.5	19.25
Average yearly g m^{-2} yr^{-1}	43.8	34.13	7.03
load kg ha^{-1} yr^{-1}	438	341.3	70.26

Table 4.2A Gradient of dust fallout from urban to remote rural sites

	dust loading kg ha^{-1} yr^{-1}	Gradient relative to inner city site
urban	438	100
semi-urban	341.3	78
rural	329	75
remote rural	70.26	16

Table 4.3A Total amount of sediment in Swanswell and Wyken Pools

	Swanswell	Wyken
1. lake area	0.73 ha	2.25 ha
2. average depth of sediment from 1850	0.475 m	0.465 m
3. volume of sediment (1*2)	3467.5 m^2	10462.5 m^2
4. average density of sediment	0.5 g cm^{-3}	0.5 g cm^{-3}
5. total dry weight of sediment (3*4)	1733.75 t	5231.25 t
6. annual dry accumulation rate per year (5/143yrs)	12.124 t yr^{-1}	36.582 t yr^{-1}
7. annual dry accumulation rate per year, lake surface area (6/1)	0.17 g cm^{-2} yr^{-1} 8850.5 kg ha^{-1} yr^{-1}	0.163 g cm^{-2} yr^{-1} 82309.5 kg ha-1 yr^{-1}
8. average % organic matter	22%	9%
9. annual dry accumulation rate of minerogenic sediment per year (7-22% or 9% of 7)	6903.39 kg ha^{-1} yr^{-1}	74902 kg ha^{-1} yr^{-1}